RECENT ADVANCES IN POLYMERS

Prof. H. F. MARK

PUBLICATIONS & INFORMATION DIRECTORATE
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

Prof. Herman Francis Mark

RECENT ADVANCES IN POLYMERS

A COURSE OF FIVE LECTURES DELIVERED BY
PROF. H. F. MARK FROM APRIL 25-27, 1962
AT NATIONAL CHEMICAL LABORATORY, POONA

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FOREWORD

The development of new and better polymeric materials is today backed by well planned programme of fundamental and applied research. Amongst the several developments, the recent discovery of stereo-specific polymers has not only bridged a gap between the man-made and natural products but signifies a sensational breakthrough and a big leap forward in the progress of science.

The National Chemical Laboratory has been fortunate to arrange lectures on the recent developments in polymers by no less a person than Prof. H. F. Mark - an internationally known authority on polymers and often described as one of the chief architects of the fascinating edifice of modern polymer science.

I am also happy to learn that persons from industry and universities also attended these highly informative and interesting lectures. A printed record of these lectures will undoubtedly be of real value to those who could not be present. I feel that the useful information in these lectures will not only kindle new lights and inspire many of our young scientists but make them actual participants in the future romance of the science of macromolecules.

S. HUSAIN ZAHEER
Director-General
Scientific & Industrial Research

New Delhi
March 28, 1965

PREFACE

During April 25-27, 1962, it was the privilege of the National Chemical Laboratory to play host to Prof. Herman Francis Mark, Director, Polymer Research Institute, Polytechnic Institute of Brooklyn, Brooklyn, New York, U. S. A., who gave a series of lectures in five sittings on recent advances in polymer chemistry to an audience composed of staff members of the National Chemical Laboratory, and chemists and engineers from universities and industries who had come specially for the purpose.

The first lecture was devoted to an account of the major advances during recent years in the field of synthesis and application of macromolecules including stereospecific polymerization. The four lectures that followed dealt with the synthesis of polymers by addition polymerization, radical and ionic, and by polycondensation; the characterization of polymers by their physical and chemical properties, like molecular weight, stereo-physical and chemical properties, stereo-regularity, and finally the correlation between structures and mechanical properties of polymers.

For all those who attended, especially for many who were hearing Prof. Mark for the first time, it was a unique opportunity to listen to and benefit from his delightful exposition of some of the latest advances made in this fast growing field of research, and his famed lucidity of exposition could not have left any amongst his listeners in doubt about any topic he touched upon. He patiently explained and answered till the last questioner was fully satisfied during discussions at the end of each session. Lecturing almost continuously for three days, performing his demonstrations with facile ease, Prof. Mark earned the gratitude and admiration of all. With a view to maintain the originality and style of presentation, the lectures were tape-recorded and transcribed. It is certain that all those who attended and those who missed the opportunity would welcome these lectures in print.

S. L. KAPUR

National Chemical Laboratory
Poona-8.

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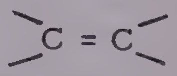
ONE

Recent Advances in the Synthesis & Application of Macromolecules

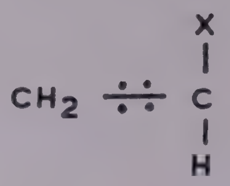
This afternoon, I would like to discuss some recent progress in the field of synthesis and applications of macromolecules, or as one also calls these materials, polymeric substances. You all know that polymer or macromolecule is the generic term of the very large family of materials which has got one common denominator. They all have very high molecular weights at least more than 20,000, often more than 1,00,000, in some cases one or more millions, and in a few cases, as much as 30-50 millions. These entities are held together by what we call chemical bonds – covalent or heterovalent – which are strong forces so that they survive many conditions such as high and low temperature, mechanical action, dissolution, precipitation, action of all kinds of chemicals; they even survive life becuase some of them are the area within which life takes place. They are in the bottles for the living cell. These basic facts are known to all and I shall just talk about some recent progress in the endeavour to produce more and more members of this very useful family. All fibres and rubbers are also high polymers. In fact, any organic substance which is a strong and hard solid is a high polymer such as wood, cotton and wool. We ourselves are substantially organic high polymers with the exception of our bones. In fact, the bones also contain some organic polymeric materials. The polymers are certainly important.

Progress in this field is continuously going on and one important question is: "In what directions does research now move in order to make more members of this family which are better and less expensive or which can be formed into certain things which have not yet been made before?" One has progressed today to the point where one does not prepare new polymers as one did twenty years ago when one synthesized innumerable cellulose derivatives because one was not sure what properties they would have. Today we have enough experience to predict the properties of a polymeric material on the basis of the structure of the monomer, the way the monomers are fitted together and how they interact with each other if they belong to different chains. In other words, we have begun to plan the properties of a polymer by planning its structure. It is an engineering problem rather than a scientific problem in the strict sense. This is of course extremely important from the practical point of view because we must not make too much random testing on what we want to get. It is also very interesting from the fundamental point of view. And now let us go to a number of specific examples and see what is now being done. Evidently progress can be achieved in two ways. We can go back all the way to the individual monomeric unit. The large molecules usually have the shape and characteristics of a chain; just like a chain consists of different units so do the large molecules. The chains are made up of units called monomers, thousand of them or may be as many as ten thousand of them fitted together. In order to ascertain the properties of such long chain molecules, we can go back to the monomer and make a new monomer, string it up into a long chain and incorporate in that chain all properties which we have incorporated in the monomeric unit by synthesis. That is the classical approach of the organic chemist. He puts in a molecule a hydroxyl group, a carboxyl group or any kind of group, the reactivity of which he wants and then strings it out into a long chain and obtains a macromolecule endowed with the characteristic properties of the monomeric unit according to plan. The other approach is to use inexpensive and readily available monomers and make new types of polymers from them. Usually these monomers are products of the petroleum industry such as ethylene, propylene, butylene, butadiene and styrene. They are put together in a new and different manner by choosing new methods, new catalysts, new experimental conditions so that when linked together, they give us macro-molecules having a different structure and therefore different properties. This second approach has been particularly successful in the last few years.

The important element of any monomeric material is a double bond or more generally a multiple bond. It is the basic element for the polymerization and with its aid, the individual monomers are joined together. In general, today when one would eventually write a double bond in such terms



indicating that there are different types of electrons which are responsible for the two bonds. By migrating to the end of the molecule and forming the links to the next unit, the π - electrons are responsible for the process of addition polymerization. This may happen in the case of $C = C$ bond or double or $C = O$ bond and the properties are not located in the multiple bond but in the substituent "X". Depending upon the



$$CH_2 \div\!\!\div \overset{\overset{X}{|}}{\underset{\underset{H}{|}}{C}}$$

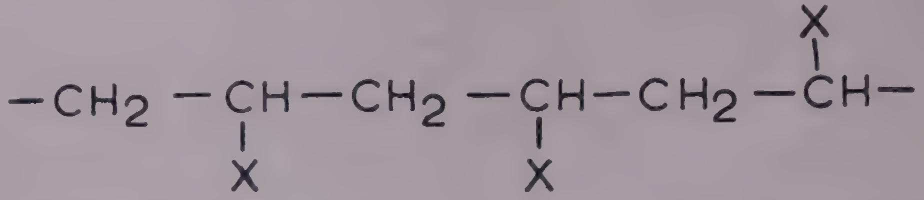
substituent, one can get solubility in water, solubility in benzene, high temperature stability and adhesive characteristics in the polymer besides its other properties. Recently, one has been particularly interested in putting in at this place (X) certain groups which permit consecutive reactions, reactions of the large molecules after they have been formed. For instance, one would like to have at this point (X), somehow an -SH group. So by putting this unit into the chain, we have here a mercaptyl group. It does not mean that the entire chain should have mercaptyl groups in each monomer. We have a chain, say, from ethylene, which is a very simple molecule which gives a very good backbone chain, but here and there, we have - SH groups attached to the chain. By copolymerization of this monomer with ethylene, we introduce into the chain these reactive groups. Now the specific advantage of this group is that upon mild oxidation, the hydrogen is taken away and a S-S bridge is formed between the two molecules wherever these groups are available. Instead of using polyethylene or polypropylene, if we use a copolymer containing a small amount (5% or so) of a monomer which has such a group and then cast the film, then by merely exposing it to air it becomes cross-linked which makes it elastic, insoluble and relatively higher melting.

Now in this special case, if one wants to get the film back with -SH groups, the S-S bond has to be reduced with a reducing agent such as thioglycolic acid or bisulphite when the cross-links are dissolved and -SH groups obtained again. So this is a way to obtain reversible cross-linking of the thin film. The one rather important application of this kind of technology is in the production of hair spray. For setting a curl, the solution of this material is sprayed on the hair which sets on simple exposure to air. Because of the cross-links, the film is resilient and rubbery and keeps the curl alive. For setting a new curl you just wash it off with a reducing agent and try it all over again. Now this is a very romantic application but this technique is also used in industrial units, mainly in the printing industry. A monomer of the type, an acrylamide substituted with CH_2SH group is

$$CH_2=CH-CO-NH-CH_2SH$$

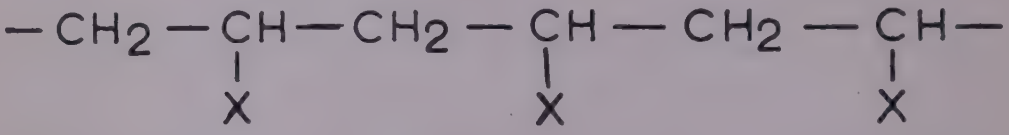
easy to make and it is a very reactive material. This -SH group easily cross-links and can be immediately uncross-linked again. It can be seen that this is the principle and instead of the -SH group any kind of reactive group can be put to suit the requirement. In the Polytechnic Institute of Brooklyn, Prof. Overberger has attached to vinyl and acrylic derivatives groups such as epoxy, ethyleneimine and isocyanate which are very reactive. As a result of this work any kind of reactivity can be incorporated in a macromolecule by co-polymerization with a specially designed monomer which brings this reactivity into the chain. The other approach is to go back to the well-known simple inexpensive monomers and try to get better polymers from them and this has been particularly successful, in the last ten years or so because of the introduction of new types of catalysts and new types of reaction mechanisms in the polymer field. We have a simple and reliable polymeric material for instance from an ethylene molecule which just has a double bond and nothing but hydrogens as substituents. Ethylene in the United States costs just about 4 cents or one-fifth of a rupee per pound. Polymerization is a relatively inexpensive process and we can make polyethylene for 15 cents a pound which is not costly, so that the product can be sold for 25 cents per pound. In the United States, polyethylene can be actually obtained at 22-23 cents per pound and that is very inexpensive. In other words, these materials are very commendable because of their low cost. But even though we take a particular material for injection moulding say, polethylene,which is strong, elastic, has a high impact strength and can be easily moulded, the main trouble with it is that its melting point is a little bit low and it is a little bit greasy to touch. Also it is not quite rigid, it is stretchable, but a kind of tough material. The next thing would be to try to use the carbon-oxygen bond; in other words, the operation is carried with favourable cycle instead of with ethylene. Formaldehyde has also got a double bond and its polymerization is also not very expensive. In other words, one can make polyformaldehyde also for 25 cents a pound. It took long until formaldehyde was successfully polymerized into a high polymeric material. Actually, almost thirty-five years ago, Professor Staudinger in Germany took to polymerising formaldehyde to high molecular weight materials but could not reproduce the reaction because there was something which was always uncontrolled. Some ten years ago, the Du Pont company took up this problem and made a very thorough study of the mechanism of polymerization. They found that the reason for the erratic behaviour was the presence of a very little amount of water in the formaldehyde monomer which has to be well dried in order to be polymerized.

Styrene and propylene are inexpensive monomers. It has been possible to improve the regularity of the structure of their respective polymers by the application of certain catalysts discovered by Prof. Ziegler. If you have a long chain of this type, every alternate carbon atom carries a substituent 'X'. If this structure is projected into three



$$-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\overset{X}{\overset{|}{CH}}-$$

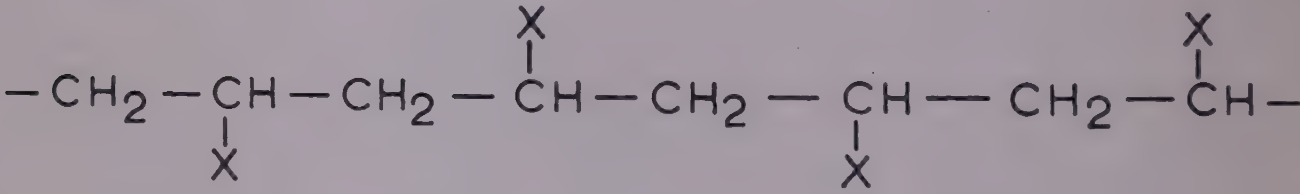
dimensions, the substituents can have a d or an l type attachment to the carbon atoms of the chain. Evidently, we can imagine a chain where all the substituents are on one side, either all d or all l as shown in structure (A). This is what Professor Natta has called 'isotactic'. The other possibility, evidently,



(A)

$$-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-$$

is that substituents would alternate regularly in the way, shown below in (B)



(B)

$$-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\overset{X}{\overset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\overset{X}{\overset{|}{CH}}-$$

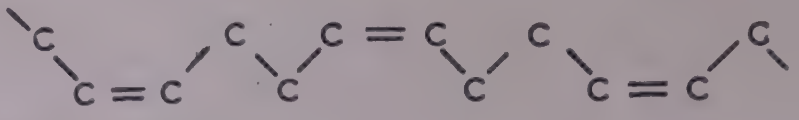
i. e. first is l , the second is d, the third is again l and so on and this is the other type of regularity which Professor Natta has called 'syndiotactic'. Of course, there is also another possibility that there is no regularity at all and the system may form a spectrum of an intermediate case which Natta has called 'atactic'. So we must distinguish between actually three types of polypropylene, 'isotactic', 'syndiotactic', and 'atactic'. All the three types have been made; 'isotactic', and the 'syndiotactic' have about the same properties whereas 'atactic' differs very distinctly. Stereoregulated types, 'isotactic' and 'syndiotactic' chains, fit well together. It is evident that if the structure has a certain regularity, the fitting will be good and as a consequence, the material will be something rigid, hard, strong, abrasion-resistant, not easily soluble and will have a high melting point. On the other hand, if the substituents are randomly arranged along the chain, then the material will be soft, low melting and so on and this is precisely what has been found. The most important polymer of this type, of course, is isotactic polypropylene, because, it is easy to make and again a most interesting point is its low cost. This is by far the cheapest polymeric material out of which one can spin a useful textile fibre and that is the reason why there is so much interest now in this specific polymer.

One very interesting application of isotactic polypropylene is in the form of films. The film of this polymer is absolutely transparent, more rigid than that of polyethylene and has a distinctly higher melting point. Similarly, isotactic polyethylene film is transparent and highly rigid and makes an excellent insulating material.

Strong fabrics that are not easy to tear have been made from isotactic polypropylene. They are being used commercially mainly for mosquito screens. Further, attempts have been made to produce multi-filament yarns which have remarkably high strength. A multifilament yarn consisting of some twenty individual filaments of isotactic polypropylene is quite strong and light; one pound of it produces a large length of fabric. Fabrics have been made from pure isotactic polypropylene purely on an experimental basis so as to evaluate its various characteristics and determine its applications. Its dyeing is not quite easy because it has a hydrocarbon chain, but it can be dyed in appropriate ways. Because of these considerations and the fact that it is a little bit hard, it is not considered as a very good fibre. However it is excellent for blending. Hence, it can be made into staple fibre and then mixed with another fibre and then spun. A blend of 65 per cent polypropylene and 35 per cent wool makes a rather good fabric. It has got much more abrasion resistance than pure wool, is very soft as compared with pure polypropylene itself and has a very nice combination of properties. A blend of polypropylene and cotton is particularly interesting for India because this cotton-polypropylene blend works very well. It has very good properties and particularly if one uses short staple cotton which is the one abundantly available in India. One cannot ordinarily spin out a short staple cotton to a fine denier but if one blends it with 60 per cent polypropylene cut to a long staple, then the polypropylene carries the cotton with it resulting in a very find denier when spun out in 110 or 120 counts. It is a very fine yarn with attractive properties. The yarn dries very fast, has got better crease resistance than cotton alone and has a very much better dimensional stability in a moist atmosphere; whereas cotton absorbs water quite a bit and therefore shrinks and expands, polypropylene does not absorb water at all. Polypropylene-rayon blends out very well. They are very light and good looking fabrics with polypropylene providing for strength, lightness, crease-resistance, and abrasion resistance. Above all, because of its low cost, polypropylene fibre eventually will be even less expensive than cotton or other synthetic fibres. Large quantities of polypropylene will be available very soon for moulding, extrusion, casting of films and spinning of filaments.

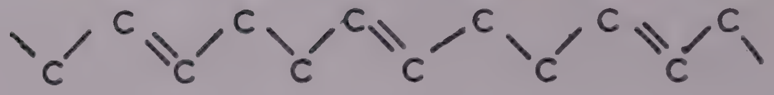
It has been estimated that in 1962, 150,000 tons to 200,000 tons of polypropylene would have been produced in the United States - quite a large quantity for such a young product. Materials such as, styrene, acrylonitrile, polyvinylalcohol which can be stereoregulated, have always, as a consequence, improved characteristics. The Ziegler type catalyst, also permits co-polymerization of materials which do not otherwise co-polymerise or do not co-polymerise smoothly. Thus, ethylene and propylene can be co-polymerized with the Ziegler catalyst, though they could not be co-polymerized by other catalysts before. Styrene and acrylonitrile can be co-polymerized and copolymers of styrene and acrylonitrile have interesting properties. Polystyrene is a good-looking transparent resin but somewhat brittle. If one co-polymerises styrene with a small amount (10-12%) of acrylonitrile, then it is not brittle. Glasses or tumblers or whatever we make out of them are practically unbreakable and they are now gradually replacing the old styled polystyrene materials which break easily.

Now, another interesting type of stereoregulation was found to exist in the domain of dienes. If butadiene is polymerized, one gets a chain wherein the double bond can be in cis form (I) or trans form (II).



I

1,4 – CIS



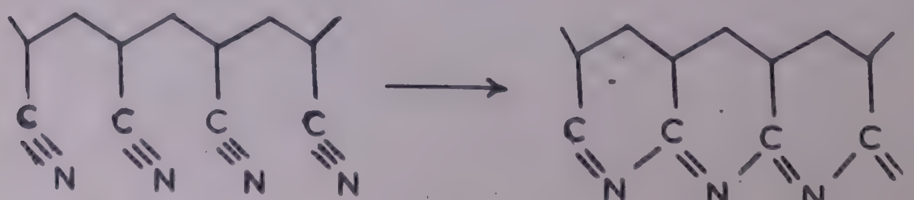
II

1,4-trans

With any macro-molecule, where we have 500 or 1000 bonds or more in succession, the differences are very drastic and very recognizable. The differences exhibited by using cis or trans polybutadiene, can be shown by preparing rubber balls of these and demonstrating their properties. Cis-polybutadiene is a nice elastic rubber. Using the same monomer but different catalysts, different products can be obtained. Trans form is a hard resin, crystalline, m.p. 80°C. and the cis form is soft, rubbery, amorphous and melts at – 10°C. or so. The same is true for isoprene, the monomer which has one methyl group. Again, we have both cis and the trans structures. The cis material is soft and elastic, whereas the trans material is a hard resin.

Natural rubber is about 88 per cent cis and it is a good rubber but not quite as rebounding as the cis-polyisoprene. The standard synthetic rubber, a styrene butadiene copolymer which is being made for years in several countries, is very similar to natural rubber in rebound characteristics. The ethylene-propylene copolymer made by Zeigler catalysts has the same rebound characteristics as natural rubber. Thus we have a series of materials with characteristic differences in their rubbery properties brought about by structural differences introduced by new catalysts.

We will now discuss the high temperature stability of polymers. All the materials which have been mentioned till now, in fact all the materials which we have already in use, go to pieces between 250 and 350°C. and the question arises, could we not make some of them very much better than that, so that they stand up to 1000°C. or above? Well, there we have to ask ourselves under what conditions are organic compounds resistant to temperature and the answer is, the more the conjugation in an organic molecule, the higher is its stability by resonance, so that we have to go back to systems like anthracene with condensed multiple ring systems in which we have to bring about a linear character, i. e. we must have linear condensed ring system. A well-known commercial material polyacrylonitrile, when heated with an acid catalyst, is converted as follows:



One electron pair moves converting a triple bond to a double bond and we get rings formed. The material in the form of a fibre or sheet by acid treatment is cyclised first and then at higher temperatures, hydrogen is split off and the system is aromatized. So here, we have a ribbon type molecule, a ladder molecule, which is highly stabilized by its molecular resonance. This material is a kind of coal really, does not contain much of hydrogen but contains nitrogen and is essentially a graphite as a consequence of which it is dark in colour. It is a graphite where we have avoided two dimensional linear lattice structures and given a certain preference in one direction. On heating, it gets pretty warm but it does not burn. So, the high degree of aromatization plus linear structure of the large molecules, enable the material to withstand high temperatures without melting or decomposition. Of course, they are of interest for work in rocketry. In rocket engines, one needs materials of this type to protect the metals from melting. Mainly in space ship construction for the nose cone protection of the returning space ships, one needs layers of these materials. Any metal would melt, as the temperature is about 4000°C. and above the metal surface one applies a thick layer of such a resin which very slowly burns off but during those few seconds, it gives enough protection so that the metal does not melt. As a fibre, polyacrylonitrile is very good looking, soft, and can be knitted into a sweater - or woven into fabrics.

Another example of a high melting material is a nylon type substance which is made from terephthalic acid and p-phenylenediamine. It consists essentially of aromatic rings which are linked together through very stable -CONH- bonds, without any additional weak links and as a consequence, this polyamide can be spun into a fibre or cast as a resin. It may be pointed that if one starts making it like conventional nylon, one runs into difficulties. For example, Nylon 66 is prepared by taking hexamethylene diamine and adipic acid both crystalline powders in a kettle, melting them, heating under vacuum, and driving off water when the polymerization takes place. One has to keep the temperature at 250-260°C. all the time in order to keep the polymer in the molten state. Now if one does the same with these two monomers, terephthalic acid and p-phenylenediamine, after a short while crystallization of the low molecular weight species takes place. They are so insoluble and so high melting that one cannot keep them in a molten state. Thus one cannot use the normal method of producing polyamides to make these high temperature resistant materials; and of course it is not surprising that if we deliberately choose our monomers such that the polymer would not melt, we cannot expect the reaction to go on. Well, in such cases, one prepares the molecule in such a manner that it is always precipitated out. If we take terephthalic acid chloride in an organic solvent say $CHCl_3$ or CCl_4 and the diamine in water and pour the aqueous diamine above the solution of the acid chloride and then at the interface the reaction starts forming the molecule which remains at the interface without dissolving in either lower or upper layer. The carboxyl end groups of the polymer at the interface can react with the amine from the aqueous layer and the amino end groups with the acid group from the organic phase below. As soon as we bring these two solutions together, the reaction stops and nothing happens any more because a polymer film forms immediately and separates the two layers. Now if we pull this film away, we can continue the reaction and in a very simple manner one can produce a very high melting, insoluble, strong, heat-resistant polymer. Of course, the polymer contains adhering unreacted monomer which will have to be washed off and that is why this method is rather wasteful. This material is actually in the market as HT-1, high temperature resistant nylon.

I think it is a bird's eye view of what is going on in the frontiers of polymer science, a very qualitative review. However, in the successive four sessions, we will discuss in detail every individual phase of the synthesis, characterization and application of large molecules.

DISCUSSION

1.	Dr. R. V. Subramanian:	You mentioned that Ziegler catalysts are used to polymerize acrylonitrile and styrene. Is it not true that the conventional Ziegler type catalysts are destroyed by acrylonitrile, then how are styrene and acrylonitrile polymerized?
	Prof. Mark:	Yes, of course the classical Ziegler catalysts comprising aluminium alkyls and titanium compounds are destroyed by monomers like acrylonitrile and methacrylate esters. But if one uses other Ziegler type catalysts, say, $VoCl_3$ and BuLi, then the copolymer is possible.
2.	Dr. P. K. Bhattacharya:	Why does a polymer chain stop growing after reaching up to a certain molecular weight?
	Prof. Mark:	Usually it is a growing free radical which by termination forms the dead polymer. Hence the higher the concentration, the faster the interaction of the radicals to form polymer by termination.
3.	Dr. G. Narsimhan:	In interfacial polymerization, how does one control the molecular weight of the polymer which is being continuously drawn out?
	Prof. Mark:	The molecular weight is controlled by two factors: (1) concentrations of the reactants, and (2) the rate of removal of the polymer formed from the interface.
	Dr. G. Narsimhan:	But reactant concentration will be a function of diffusion to the interface.
	Prof. Mark:	Yes, but the concentration gradient will determine the diffusion and original concentration will determine one end of gradient and rate of removal of polymer, the other end of gradient. It is all neatly worked out but there is a lot of wastage (say only 60% polymer yield).
4.	Dr. R. Ananthakrishnan:	What determines the transparency or otherwise of plastics?
	Prof. Mark:	The order of crystallinity determines transparency.
	Dr. R. Ananthakrishnan:	How do the refractive indices of plastics compare with those of glasses?
	Prof. Mark:	The values are between 1.47 and 1.52 for plastics. Plastics are not suitable for high precision optical instruments. But in some applications, plastic lenses are replacing glass.
5.	Dr. G. S. Kasbekar:	Polyethylene industry in our country is based on alcohol. Do you think it will have a future when petrochemical industry is established?

Prof. Mark: It is a question of economics. If the refinery ethylene is of lower cost, then naturally it will be used. But ethylene from alcohol is very pure. In India, I hear that alcohol-based ethylene plant for styrene-butadiene rubber is being put up at Bareilly.

6. Dr. Kartar Singh: Is it possible to replace compressed air by foam rubber?

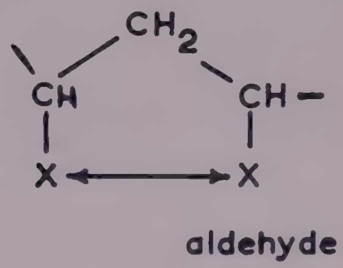
Prof. Mark: Attempts are being made to replace it with foam rubber but lasting properties and comfort are not satisfactory. Nothing so good as compressed air as yet.

7. Dr. H. C. Subba Rao: Is 'high temperature geon' PVC stereo regulated PVC? In which way is its manufacture different from that of normal PVC?

Prof. Mark: Yes, 'high temperature geon' is stereoregulated and it is made by using as catalyst a combination of an aldehyde, e. g. butyraldehyde and peroxide.

8. Dr. R. V. Subramanian: Is the function of the butyraldehyde and peroxide catalyst system only to bring about free radical initiation? If so, how is stereoregulation achieved in vinyl chloride polymerization with this catalyst?

Prof. Mark: One does not know for certain; but probably it is a type of complexing at the growing end of the polymer radical of the aldehyde which leads to a definite conformation during addition of a monomer unit.



TWO

Synthesis of Macromolecules - I

Addition Polymerization

The first two sessions, we will devote to the synthesis of macromolecules. Now, in making large molecules from small ones, there are essentially two considerations in the beginning at least, viz. rate of polymerization and molecular weight of the polymer. So what are the present possibilities of controlling these two factors? Any formation of a large molecule involves the reaction of small ones with one another. There are essentially two types of processes which are used. One is a reaction known as Addition Polymerization where the monomeric unit is endowed with the capacity to develop reactivity which provides for successive addition of the same molecule or group of similar molecules to each other. The other is the so-called Condensation Polymerization where the material is endowed with bifunctionality in such a manner that by a successive continuation of reaction between functional groups, large molecules are formed.

Addition Polymerization and Condensation Polymerization are not strictly different. There are cases like the polymerization of ethylene where there can be no doubt that it is a clear - cut addition polymerization and the cases like the reaction of hexamethylenediamine and adipic acid where there is no doubt that it is a condensation polymerization which proceeds gradually with the elimination of water. But there are over-lapping cases like the formation of polycaprolactam from caprolactam where one does not exactly know whether it is an addition polymerization or a condensation polymerization. The type of polymerization is clear in some cases and it is rather vague in others. Let us consider those cases when the type of polymerization is very clear.

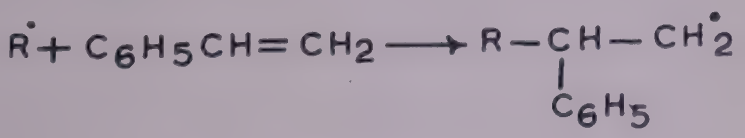
The essence of addition polymerization is that we operate with a molecule which has a multiple bond or to express it a little bit more in modern language, which has π - electrons, i. e., electrons which occupy certain orbitals in the molecule which are not so close to the nuclei. Usually we indicate these π-electrons by two little dots although we know that electron is not localized and it is not localizable but to draw a diffuse cloud into a formula, will be confusing; so this is a shorthand expression. Now, these π-electrons have a certain energy level and since they protrude with their electronic density quite far away, about 1.5 Å away from the axis of the molecule, they are susceptible to the attack by another molecule and that is naturally why we call them reactive. In order to stimulate this reactivity, one can use different means. One can stimulate the reactivity of the π-electron with a free radical with one unpaired electron but one can also stimulate it even with the positive or the negative ions. So, there are essentially three types of stimulations for the reactivity of electron of a multiple bond, viz., free radical, ionic cationic, and ionic anionic. Let us consider one after the other the most recent developments in these respects.

In order to initiate the reaction of this type with free radicals, it is necessary to make free radicals and the question arises as to how we make free radicals in an organic solvent or in the aqueous system. Well, somehow, we have to break a molecule into pieces in such a manner that there remains a lone electron on each of these pieces. Now arises the question, what are the most convenient molecules to use for this purpose? Certainly, ethane, benzene, methane would not be convenient because their dissociation only occurs at very high temperatures where the large molecule which we want to form would go to pieces. We actually look for organic molecules which have the tendency to dissociate well in this manner at low temperatures if possible at − 100° to 60° C. In other words, we would like to have a convenient array of free radical formers through the decomposition of the organic molecules and this is one branch of organic chemistry of macromolecules which provides permanently better and better materials of this type. Historically, attention was drawn to the decomposition of peroxides and one popular type is benzoyl peroxide and it was found many years ago that benzoyl peroxide when heated in a solvent like toluene or xylene, liberates CO_2 and gives a fair yield of diphenyl. When this reaction was studied in terms of the individual steps, it was found that this peroxide bond breaks first, because by adding any material which has an easily abstractable hydrogen atom, it was possible to get a considerable yield of benzoic acid. So the first thing is that the peroxide dissociates and the phenyl radicals abstract the hydrogen atom from somewhere or if they do not find anything, the free radicals eventually decompose and CO_2 comes out and then two benzene radicals dimerize and form biphenyl. From this kinetic analysis, it was possible

$$C_6H_5COOOCOC_6H_5 \rightarrow 2C_6H_5COO^{\bullet}$$

$$\rightarrow 2C_6H_5^{\bullet} + 2CO_2 \rightarrow C_6H_5{-}C_6H_5$$

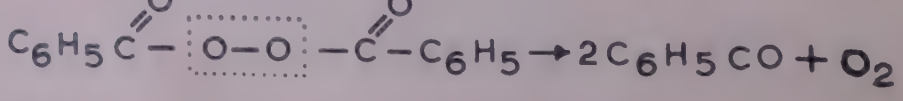
to estimate the concentration of free radicals at any temperature and it was found that it was very low, between 10^{-6} and 10^{-8}, so that for normal purposes, the transient existence of this free radical has no importance. But if we add to this a monomer molecule, then we immediately get a secondary reaction, namely the attack of the free radical on the electron pair of the monomer, and what happens is that the free radical R interferes with one of these two π-electrons, forms a normal sigma bond and the other electron is relegated at the end of this atom as shown below.



$$R^{\bullet} + C_6H_5CH{=}CH_2 \longrightarrow R{-}\underset{\displaystyle C_6H_5}{\underset{|}{C}H}{-}CH_2^{\bullet}$$

In other words, what happens in this process is that an electron pair cascades down from its π-energy level to the sigma level, the two electrons are unscrewed and each of them becomes a sigma electron. There is an energy difference of something like 20 kilocalories between the triplet state of the level and the singlet state of the sigma level. This process therefore is quite exothermic.

The first process, of course, i. e. the dissociation of the peroxide is endothermic; in fact, the order of magnitude of the energy needed to dissociate the benzoyl peroxide is 30 kilocalories and this free radical attacks the monomer molecule in this first step, reproducing a free radical which attacks the next monomer and so a chain reaction develops. Each subsequent step is the cascading down of a π-electron pair to a sigma electron level, so that each step gives about 20 kilocalories per mole. With a very small amount of energy invested here, we have got to dissociate only one molecule to get a very large amount of energy from the system because of its reactivity. This is precisely what happens when one lights a flame with a match. Peroxide is a match and radical is the flame and as long as there is monomer around, the flame will go on and only after all the monomer is consumed, is the process at an end. We thus capitalize on the high reactivity of the multiple bond, initiate the reaction by one kickoff and then it runs all by itself because of its exothermicity and because of the fact that there is still monomeric material available for the continuation of the reaction. The reactions of this type are known as chain reactions and all addition polymerizations are typical chain reactions. The mechanism of chain reactions of all kinds, not only of this kind, has been studied very thoroughly for many years. The main exponent of this science has been Prof. Semenov in Moscow who has written a classic book on chain reactions and who has also been awarded the Nobel Prize for his work. Normal chain reactions involve the transfer of energy to the next step of the process whereas in this chain reaction the next monomer is added to the growing macromolecule. So here, we actually get a chain as a result of the process. For many many years, one started the chains and let them grow the way they wanted; but what is the end, when does it stop ? Only after all the monomer is consumed? Well, the answer is 'NO'. There is another reason for cessation of individual chain growth. If we have a free radical chain growing up to a certain length and if we have another free radical chain growing up to a certain length, there exists a certain probability for these two chains to collide with each other. And if they do collide, they react with each other. These growing radicals pair up or disproportionate and the reactivity is lost. So there exists a termination as such, extinguishing all the flame. This makes it necessary that we keep it alive all the time by additional production of new free radicals. The molecules of peroxide which we are using as initiators decompose in the system to give new free radicals which start new chains. It is rather a simple picture. It is a system where a number of catalyst molecules because of slow decomposition, slowly provide the free radicals. We have a monomer which immediately takes those free radicals, grows them out to chains and eventually terminates them. And these three processes - initiation, propagation and termination — fit into each other and it is quite easy to write down the book-keeping for such a process in terms of a few differential equations for rate of free radical formation, rate of propagation and rate of termination. And on the right side of these three equations we have the concentration of catalysts and the monomers and of course we have the temperature. So the kinetics of these processes have been worked out many years ago and is something which has been developed quite a bit in detail. The next step is to provide a large number of molecules, simple organic molecules, which would decompose in some solvents at certain temperatures with certain speed. For a while attention was centred on peroxides; then it became evident that there are other materials available. In fact the peroxide has one disadvantage that there is also another type of decomposition, namely oxygen breaking off and the peroxide acting as an oxidizing agent. Other materials available are



$$C_6H_5\overset{O}{\overset{\|}{C}}-\boxed{O-O}-\overset{O}{\overset{\|}{C}}-C_6H_5 \rightarrow 2C_6H_5CO + O_2$$

azo compounds which should break at -N=N-, diazoethers which break at =N-O-, diazo-thio-ethers which break at =N-S- and so on. In other words, there exists today a dozen types of small organic molecules which can be induced to produce free radicals of all kinds. This has very greatly facilitated the operation in many cases. In some cases one wants to work at high temperature, let us say we have a monomer which is crystalline at room temperature and which melts only at 150°C. difluoro- and trifluorostyrene, and if one wants to polymerize the monomer in the melt, then we need a catalyst which melts only at 150°C. And it must not decompose too much because if it produces too many free radicals, we have a very rapid reaction, yielding only short chains, since too many free radicals terminate each other quickly and the individual chains have no chance to grow up to considerable length. So, if we want to get a high polymer of trifluoro styrene at 160°C., we have to have a catalyst which at 160°C. only decomposes to about 10^{-6} of its concentration; there are such catalysts. But once we understand the process, we can intelligently plan for better auxiliaries, better materials to help us make the big molecules. It has been found that in many cases polymeric materials have an irritating effect on the human skin. This has been found not only in nylon but also in polyethylene used in very large quantities, as a packaging material. We have something packaged in polyethylene, we carry it in our hand or in pocket and then suddenly we feel a certain irritation. Now, of course, the reason for that has been very carefully investigated and it has been found that the macromolecules themselves, polyethylene, polyamides, polyesters, etc. have no irritating effect on the body because they do not penetrate the body; they are too large. The entities that cause this irritating effect are always small molecules which eventually diffuse into the skin and which do irritate the skin and they come sometimes from remnants of the catalysts. It is known that only 10^{-6} or one millionth of the total catalyst used decomposes and the rest is there only as a supply to keep the reaction running so that if we started with one gram peroxide, we will have most of it left even after secondary decomposition in the polymer. Well, benzoyl peroxide has certainly some irritating effect.

So an important step in the preparation of every polymer is the removal of the remnants of whatever ingredients are used in the preparation, viz. catalysts, modifiers, stabilizers. This has to be done by washing or dissolving and reprecipitation and that is the reason why in any calculation for the cost of a polymeric material one always finds a large amount of money set aside for the finishing or the cleaning of the polymeric material. This is the present state of affairs in the choice of materials for free radical polymerization but free radicals can also be produced without any decomposition of a specially added substance i. e. by light, by photons. Photons which have sufficient energy can abstract an electron and so they leave another electron unpaired and therefore photo-initiation has been always studied with interest. The great advantage of photo-polymerization is that free radicals can even be produced at very low temperatures. With ultraviolet light or even with gamma radiation, it is very easy to produce free radicals at any temperature - say even at −200°C. And therefore, a new branch of polymer science is the study of addition polymerization at very low temperatures initiated by either gamma or beta radiations. Usually one uses one of the waste products of a nuclear reactor either cobalt or whatever isotopes one wants to take. And then we have a crystal of monomer, say of propylene at −180°C. or −150°C. and then a gamma ray goes through producing a photo electron which further produces a number of secondary and tertiary electrons forming what is known as a 'square' which is full of reactive particles and of electrons. Many of them recombine immediately after a micro-second or so but one or two or three of them start to react with the monomer and they grow chains. These chains keep growing and this is the manner in which one can get almost any unsaturated material to polymerize at low temperatures without any catalyst. Many scientists are studying it at present very vigorously because eventually this might be quite an inexpensive way of doing it; cooling does not cost much more than heating if it is done on a large scale and good insulation is possible and the advantage is that the polymer is absolutely pure, as pure as the monomer. Nothing is added. Solid state low temperature polymerization is a very interesting field of fundamental and industrial research.

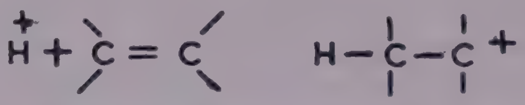
Now that much about free radical initiation. We should put also a little bit of mathematical book keeping given below just to show how simple it is. The great advantage of a number of equations which describe and quantitatively embody such a process is that if we look long enough at them, we get a few ideas of how one can run a reaction better. One can see immediately from the equations what influence each of the factors has on monomer concentration, catalyst concentration, temperature and so on.

$$R_p = \frac{K_p\,[M]}{K_t^{1/2}}(K_d\,fI)^{1/2}$$

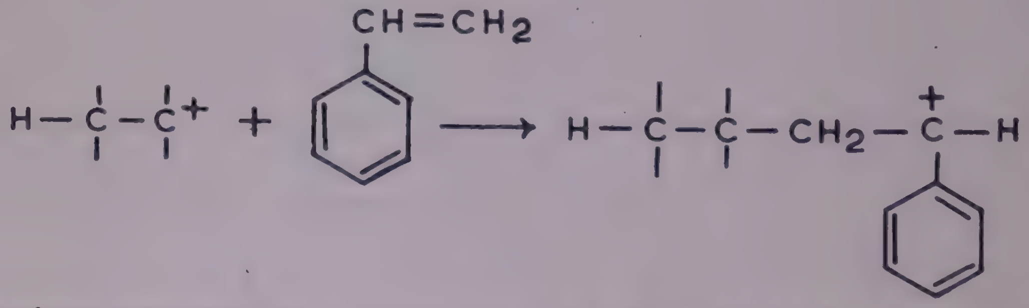
$$\delta = K_p^{2}\,[M]^2/2\,K_t\,R_p$$

where R_p is the rate of polymerisation; K_p and K_t are rate constants for propagatio and termination; K_d is the rate constant for decomposition of initiator; δ is the chain length; f is the factor for efficiency of initiation; [I] and [M] are concentrations of initiator and monomer respectively.

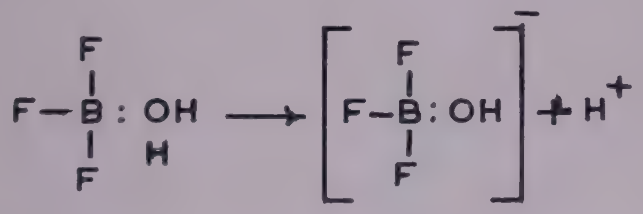
Now an electron pair - a π -electron pair, however, can also be stimulated to reactivity in other ways. One can approach this system with an ion, say with a proton which pulls the two electrons over to it and a positive charge is transferred to the far end and we get a carbonium ion.



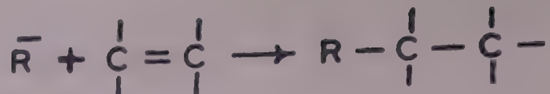
With a vinyl monomer like styrene, the carbonium ion attacks the monomer and again the stage is set for a chain reaction.



But now this chain reaction does not involve the divorce of the electron pair - it only involves the displacement of the electron pair, so that all we do in an adiabatic fashion is that we pull the charged cloud of the electron pair over and let it condense into the charged cloud of a sigma electron pair. Again we have a cascading from the triplet level of the π to the singlet level of the sigma which is exothermic. So, the initiation takes place by the attack of a positive ion and by the displacement of the electron pair in the direction of the positive ion, i. e. a cation. Well, whenever there is a cation, there must be an anion. So, somewhere in the system, there is an anion and evidently the anion always must be in the neighbourhood of the positive charge, because they attract each other. This process takes place in an organic solvent, benzene, toluene, xylene, etc. so that as the chain keeps on growing and as the carbonium ion keeps on moving, the anion all the time runs along like a watch-dog and stays always in the neighbourhood of the growing chain so that the chain end always is an ion pair, cation at the end of the growing chain and anion opposing it. What is the termination in this case? Evidently, the termination is when this ion-pair precipitates out, as when an insoluble salt is formed; and by choosing the right anion which forms no insoluble salt, eventually this kind of process can be kept going on for a very long time. In other words, this anion is very lazy and if the solvent and the temperature are such that these two charges remain always separated, then polymer keeps on growing, until there is no monomer left. Conditions of this kind have been actually found and established by Prof. Szwarc for growing anions and he has called polymers which are made under such conditions, as "living polymers" because they keep on growing as long as they have food available. If we change the temperature or add another solvent then this might immediately stop further propagation by the formation of salt so that in the case of a cationic initiation, we must produce an ion pair. Then if the cation happens to attack the monomer, from then on the process is again a highly exothermic chain reaction which goes all by itself and we have the chain of high molecular weight by the proper choice of the counter ion and of the solvent and eventually of the temperature. How do we get ions in an organic solvent? In general, of course, in an organic solvent there is very little dissociation. But if we choose materials which are particularly polar one gets just enough. After all we do not want much, we only need one in a million. So, for instance, if we have boron trifluoride with a very small amount of water then we know that BF_3 hydrate is formed. Boron attracts the electron pair on the



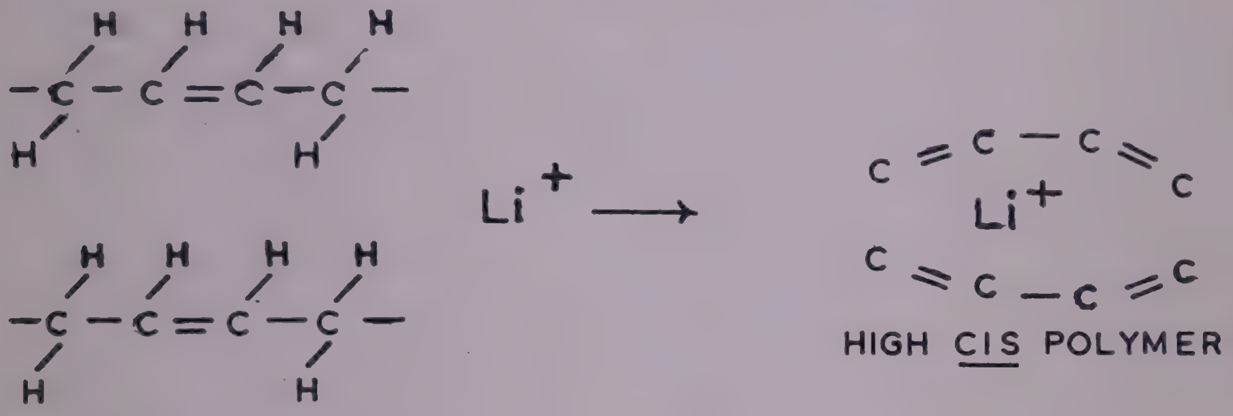
oxygen loosening the bonding between oxygen and hydrogen which hence has a tendency to dissociate off in the form of a proton leaving the negatively charged BF_3 hydroxylate as the counter-ion. This cation, proton, starts the chain forming through the carbonium ion, and $(BF_3OH)^-$ is the anion which always faces the growing chain end on the other side. If there is no water present, the reaction does not proceed. If it must not be water, it can be methanol; any kind of compound which under the influence of BF_3 dissociates off a proton is a cationic catalyst. So that a cationic catalyst always consists of two parts, of the proton donor and of the components which loosen up the proton, facilitating the donation. This is what is called Lewis acid and anything of that kind, BF_3, $AlBr_3$, $AlCl_3$, can be used and is actually being used as a cationic catalyst. Now, the third way of getting a chain reaction of this type going is through an anionic catalyst and let us go back again to our monomer which can have a carbon-carbon double bond or a carbon-oxygen bond, as in an aldehyde. And let us now approach this by a negative ion, that is to say by an anion which has an exposed electron pair. Somewhere in the molecule there is a protruding orbital of negative electricity representing an electron pair which is negatively charged. In other words, there is one excess electron in the whole system. Then of course this electron pair, this negative charge, can push the π-electron pair in the molecule as far away as possible, that is to the end of the molecule, forming at the same time a sigma bond with the molecule which becomes another anion. So we have again an

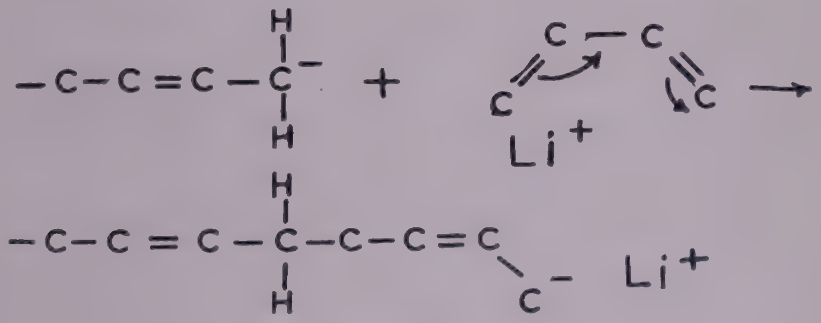


$$\bar{R} + \overset{|}{\underset{|}{C}} = \overset{|}{\underset{|}{C}} \longrightarrow R - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} -$$

electron displacement: the electron pair displacement process where the strongly negatively charged anion pushes the π-electron pair of the double bond down into sigma electron level and it is all negatively charged. In other words, this fact of propagation means the motion of an electron pair in the direction of the growth, whereas the cationic propagation means the motion of the electron pair opposite to the direction of the growth. Now again the cation will always be close to the anion and while the chain grows again the cation moves along. Now these ionic type polymerizations are also chain reactions and again the termination will be the formation of insoluble stable compound between these two positively and negatively charged parts. How can we make a reactive anion ? This is usually done either by using metal alkyls or by using the metals themselves. The cleanest way of initiating anionic propagation is to use a metal alkyl, soluble metal alkyl, and a particularly clean-cut and simple material is lithium butyl. This is a liquid, reactive but not too reactive. It is convenient; it does not burn and we can add it to any system we want to. Sure, water and oxygen have to be absent. We have to use normal cleanliness but do not have to be supercautious. And therefore, lithium butyl, amyl lithium or amyl sodium and a number of metal alkyls are used as anionic catalyst, whereas Lewis acids are used as cationic catalysts. In the case of lithium butyl, of course, butyl anion starts the chain and lithium is the counter ion. Now, both these types of anionic and cationic initiation are in terms of the mechanism, in terms of the kinetics, very similar to the free radical type but in terms of the absolute value of the individual rate constants, they are very different because the ionic dissociation does not need much activation energy. If we take lithium butyl at room temperature or even at -30°C. or - 40°C. in toluene it dissociates all by itself to about 10^{-6}; that is what we want. In other words, the activation energy for the initiation reaction is much smaller than in the case of a free radical initiation, except of course of photopolymerization. As a consequence, anionic and cationic polymerizations proceed at very low temperature. Thus, isobutylene can be polymerized very rapidly at -90°C., using BF_3H_2O or BF_3 etherate. Acrylonitrile can be polymerized at the same temperature very rapidly with lithium butyl. So the advantage here is that one can also work at much lower temperatures and naturally also at high temperature if one uses appropriate compounds. The disadvantage is that one needs an anhydrous oxygen-free system. Free radicals are completely insensitive against water. They are a little bit sensitive against oxygen but not too much. Therefore, in general, a free radical polymerization, particularly in an aqueous system like emulsion polymerization, requires much less care and much less precision, than these anionic and cationic anhydrous polymerizations. This is the reason why between 1925 and 1945 practically only free radical initiated addition polymerization was used commercially and only recently more and more cationic and anionic type anhydrous polymerization has become important and also in large scale operations.

Now this type of polymerization where we have a counter ion, provides for an additional tremendous advantage which was dimly known for many years but which became clear only through the discovery of Professor Ziegler and Professor Natta. They are now of course being carried out and expanded and amplified everywhere in the world. The main difference between certain types of ionic polymerization and free radical polymerization is that we have in the former a counter ion. In a free radical polymerization, the chain starts to grow somewhere, keeps on growing when another monomer is added to it. By virtue of the randomness of a liquid or gaseous phase, any kind of steric configuration will be of equal probability during the process of the addition. Now, in the ionic polymerization the situation is quite different. Here, we have an ion pair, with a counter ion at the growing end which somehow controls the addition of a next monomer. Let us assume that we polymerize butadiene or isoprene with butyl lithium. We end up with a negatively charged chain end with the lithium counter ion. Lithium is now complexed even without polymerization because butadiene has two double bonds and the electron pair is being attracted towards the positively charged lithium ion. Lithium is a very small ion. Therefore the divergence of the lines of force is large and the field is strong. This strong field displaces the electron pair of the two double bonds in a certain manner. So the complex has a certain stability; it is stable enough so that one can pick it up at low temperatures, both by infra-red absorption and also by nuclear magnetic resonance (NMR) studies. So this is a transient complex with two butadiene molecules forming a ring with lithium in the middle. Let us assume that at a certain moment we have this situation and then of course there is a vibration of this transition state and when there is a particular vigorous vibration, the electron pair may move to form a sigma bond and the negative charge moves to the end. Of course, lithium is going to move up along with it completing addition of the monomer to the chain.



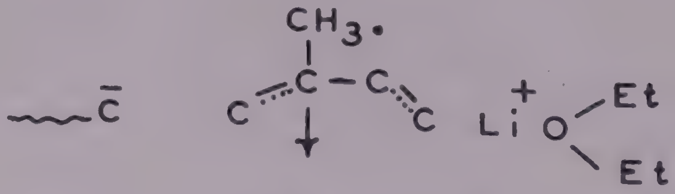


propagation step

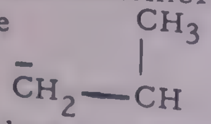
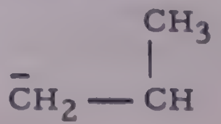
This is the individual propagation step, a little electron pair wind that blows in the direction of growth. Very little energy is necessary to do that, a little bit of vibration and the monomer is added.

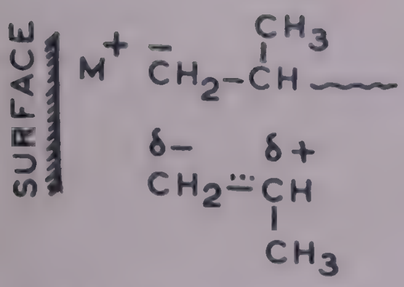
The existence of such complexes of lithium has been shown by infra-red (IR) and nuclear magnetic resonance (NMR) studies at low temperatures. If one dissolves butadiene in heptane or pentane and adds lithium butyl at low temperatures, -90°C. or so, there is no polymerization but an adduct formation.

Many years ago, Ziegler postulated such a complex not as a consequence of physical measurements but as a consequence of chemical reaction. That was then a postulate but today we have something positive. That was shown mainly by Prof. Korotokov in Leningrad. It can be seen whether one has obtained the addition in the fixed configuration. Butyl lithium actually does produce an all cis or high cis-polybutadiene or high cis-polyisoprene. Hence, the counter ion has got a terrific advantage that we can manoeuvre with it to obtain steric control by complexing of the counter ion. Today what one does for steric control of polymerization is that one studies the complexing of monomers with counter ions; because this precomplexing leads to a regulated introduction of the monomer into the chain; and this is precisely what Ziegler polymerization means. In the case of Ziegler polymer or Natta polymer, we have a rather complicated counter ion, built up from a transition metal halide and aluminium alkyls. In other words, it is a large particle; actually in many cases, this is a solid surface; so that now we place the emphasis not on the growing chain but on the counter ion which is the important thing. We get a situation here, where the macromolecule grows out like a hair from a certain place. The monomer comes in at the surface and gets caught, as the chain grows out. We have either a precipitated catalyst, or even a soluble catalyst, and the counter ion becomes large and powerful enough to surround itself, precomplexed monomers before they enter the chain and we have stereoregulation. This means control of every propagation step with the help of the counter ion. With normal free radical polymer, we have started the chains and let them grow wild, which terminate eventually somehow. But we never attempted to keep every propagation step under control. Now we do that with the aid of counter ions which form a powerful means of keeping every addition step under control sterically in terms of how the next monomer is added. In the case of butyl lithium, Prof. Korotkov has also shown a very interesting thing. With isoprene polymer, the results were rather erratic, sometimes high cis, sometimes random and sometimes high trans polyisoprene were produced. So he carefully purified all the substances and found that in the complete absence of all oxygen-containing substances, one gets high 'cis' content. But if one adds oxygen or better, ether, the diethyl ether complexes with butyl lithium. This was established in several ways in the absence of monomer also. As a result, the configuration of the complexing monomer at the growing end is altered and we get a trans addition.

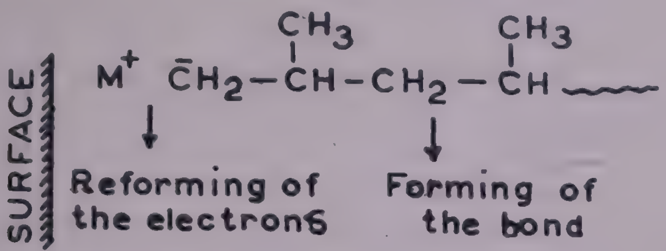


Trans polymer

Using butyl lithium in heptane, high cis polyisoprene is obtained whereas with co-complexing agents, one gets high trans. This is real stereoregulation, growing the macromolecule to a required size, as in the classical way but with almost complete control of every addition step. The other type of stereoregulation to produce the isotactic and syndiotactic types also requires the preference of a certain transition state to all others. When the next monomer molecule approaches the surface of the complex, then the electron pair of the monomer will be attracted by the charge M^+ and repelled by the - charge  $\bar{C}H_2 - \overset{CH_3}{\overset{|}{CH}}$ so that the molecule becomes a dipole, the molecule as it approaches gets polarised, the electron pair moves over M^+, causing an increase in the distance between M^+ and  $\bar{C}H_2 - \overset{CH_3}{\overset{|}{CH}}$ from 1.35 Å to 1.54 Å gradually.

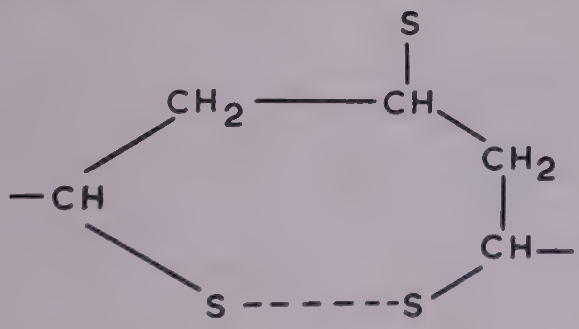


Then in potential energy landscape,as it approaches, it crawls up the saddle and as soon as it approaches the saddle, it falls down, resulting in reformation of the electrons and formation of the bond as shown below.



With this operation, isotactic and syndiotactic configurations are possible. We do not know actually why, but whatever the reason, there is a preference for the monomer coming in one of the possible configurations that gives us an isotactic material. We have, hence, cis and trans stereoregulation depending on the size of the counter ion, its structure, its charges and also the action of the other ingredients in the system which can compete with the monomer about the various positions in the complex with the counter ion. This is complicated but wonderful and the great advantage of ionic type polymerization is that we make isotactic or syndiotactic polypropylene, or 1, 2-polybutadienes when we do have a counter ion which we can manoeuvre.

But in the free radical initiation also, it has been possible to bring about stereoregulation in recent years. Syndiotactic polymethylmethacrylate can be made as Dr. Fordyce, Ham and others have found. Let us look at the two members of the growing chain of polymethylmethacrylate.



If the substituents 'S' are polar as in polymethylmethacrylate, then this ring is stabilized by the interaction between the carboxyl groups; if they are free, they form hydrogen bonds and if they are esterified, they interact by polar forces, so that there is a little complex formed. A very small plate - a little Ziegler catalyst and the next monomer approaches the growing chain because of the ring and the substituents forming the bridge, there is a preference to approach it from one side as compared with the other side and this gives stereoregulation but always syndiotacticity, because after a monomer is added, the next ring forms and the approach becomes more probable from the other side. Hence, even in a purely liquid system without a counter ion, one can produce a sufficiently high degree of molecular order in the neighbourhood of the growing chain end to get stereoregulation. It must be at low temperature and sometimes one uses an additional co-complexing agent which stabilizes this ring. And what that really means is that in a liquid at sufficiently low temperatures, there is a very high degree of local order. We always think that in a liquid, molecules are moving around completely irregularly. This is only true for larger distances. If we look in a sphere, which has got a radius of 3 Å, it is almost like a crystal. Inside such a small volume element in a liquid there is a high degree of molecular order created and maintained by the polar forces between the molecules whatever particles there are inside. This never happens with a hydrocarbon. One can never stereoregulate polypropylene that way or polystyrene or any polyhydrocarbon but one can very well stereoregulate polar monomers. The more polar they are, the better it works. Polymers like polyvinyl acetate can be got in completely syndiotactic form at very low temperatures. We are gradually getting to the details of the propagation reaction itself. In living polymers on the one hand, we avoid termination and in stereoregulation a complete or almost complete control of each individual propagation step is achieved with the aid of a counter ion which is very powerful or by the appropriately chosen local environment at the growing chain end.

These are now the most rapidly progressing fields in the area of addition polymerization. They are being studied with great intensity in all kinds of directions. Of course, these stereoregulated processes are slow but not unreasonably slow. Instead of a cycle of twenty minutes in the case of other conventional polymerizations, this takes two hours or so. We know how to bring about stereoregulation with polar monomers like acrylonitrile, methylmethacrylate, acrylates, etc. by free radical mechanism. But I do not think that we will be able to stereoregulate by free radical mechanism the polymerization of styrene, propylene, etc. unless of course one goes to very low temperatures. Very interesting experiments have been made in connection with the polymerization of propylene in the crystalline state with gamma-rays, of course, at very low temperatures. Here, stereoregulation is caused by the crystallinity and hence the difference. And, I think, this is the story in bringing you uptodate with the present state of addition polymerization, either ionic or free radical, including whatever we have learnt recently on the problems of stereoregulation.

DISCUSSION

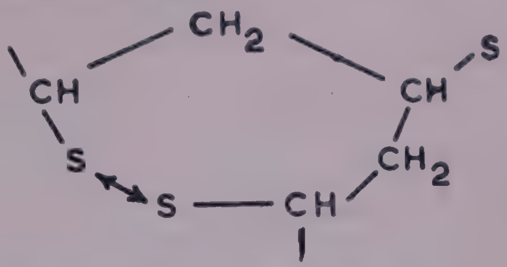
9. Mr. T. V. Subba Rao: It appears easier to make long chains and scissor them off at convenient D. P. to save time and money. Has any work been going on in controlled degradation and how far is it possible to make chains of required D. P. from longer chains?

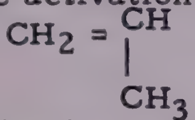
Prof. Mark: The problem is this: what is better? In fibres, you take the required molecular weight. But in rubber technology, mastication is important. If you want to blend intimately any processing material you can use blending operation for degradation from high molecular weight to low molecular weight.

10. Dr. Kartar Singh: What is the evidence for the complex formation between lithium and butadiene?

Prof. Mark: Infrared absorption and NMR studies at low temperatures about -80°C. or so have shown the adduct formation between these two. Many years ago Prof. Ziegler postulated the same idea from chemical consideration but did not have the definite experimental evidence which we have today.

11. **Dr. R. V. Subramanian:** You had pointed out that stereoregulation of polymerization at low temperature is due to complex formation and interaction between polar substituents, 'S' in proximity at the growing chain end- as shown here. Then how is the activation energy of syndiotactic and isotactic placements affected?




$CH_2 = CH(CH_3)$

Prof. Mark: The activation energy is dependent on substituents; in $CH_2 = CH(CH_3)$ for example, the difference in activation energy for syndiotactic and isotactic placements is 1.8 kcal./mol. even at 30°C. which is hence self-stereoregulating. If the difference is much less, say about 600 cals. per mole, the effect may not be observed.

12. **Dr. Kartar Singh:** Could stereoregulation be achieved by application of electrical field at low temperature in case of monomer with dipolar groups?

Prof. Mark: It is being attempted; it might be possible.

13. **Dr. M. K. Kaulgud:** What are the factors which decide whether an ionic catalyst will behave in an anionic or cationic way?

Prof. Mark: Well, it is an interesting question. One adds another substance which will react with the cation or anion. Well, if you add a cation and if the polymerisation had been proceeding in an anionic way, now it will stop. On the other hand if it was a cationic polymerization, it will not be affected at all.

THREE

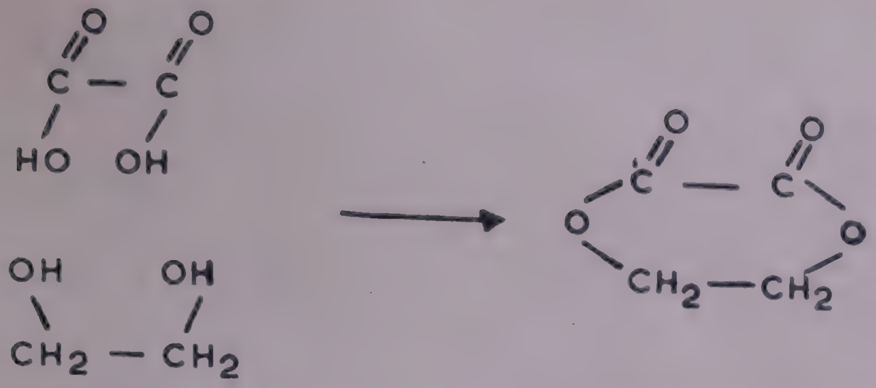
Synthesis of Macromolecules - II

Condensation Polymerization:

Condensation polymerization involves the reaction of bifunctional molecules like dibasic acids, glycols or diamines with the elimination of small molecules, usually water or alcohol. Polyamides like nylon or polyesters like Terylene are made by condensation polymerization. When adipic acid is reacted with hexamethylenediamine we get Nylon 66 and water; from dimethyl-terephthalate and ethylene glycol, methyl alcohol is split off and we get polyethylene terephthalate or Terylene. In this respect, that is, in the removal of small molecules of water or alcohol, condensation polymerisation differs from simple addition polymerization which was considered earlier, where only the monomer is added to the growing polymer chain; and it is essential for the formation of polycondensates that this removal is continuous as one works in the neighbourhood of equilibrium conditions. The process is endothermic and heat is applied to take the water away and again this is a difference from addition polymerization which is exothermic.

In polycondensation, addition of molecules of any size takes place as long as they have the reactive end groups. This is a stepwise reaction with only one reaction involved in the process, the repeated formation of ester linkages when one has glycol and diacid; or the formation of amide links if diacid and diamine are taken. In this stepwise condensation process involving the reaction of the different end groups on molecules, it is very important to precisely adjust the molar ratio of the reactants since it controls the molecular weight of the polymer formed. The purity of the reactants is also very important. Acids can be obtained in pure form but it is considerably more difficult to purify the glycol or amines which are hygroscopic. Further, contamination by monofunctional monomer should be thoroughly avoided since it would block the end groups of the polymer and hence will be detrimental to polymerization.

The other difficulty in condensation polymerization stems from the fact that sometimes formation of rings instead of chains can take place. There is always a competition for formation of rings which means two monomers are lost for each ring formed thus:



Fortunately, the formation of rings depends on the size of the resulting ring compound.

If the percentage of ring formation is plotted against the number of carbon atoms in the ring, it will be found [Fig. 1] that it is highest when the ring contains five or six carbon atoms and the macromolecule is formed only

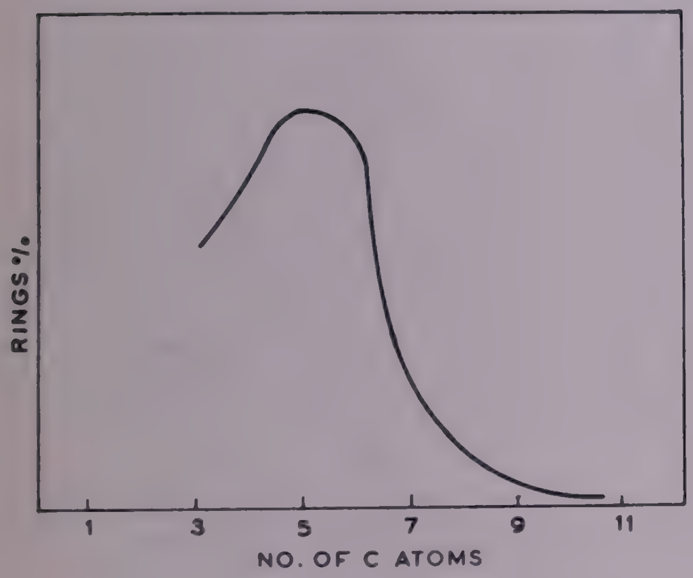
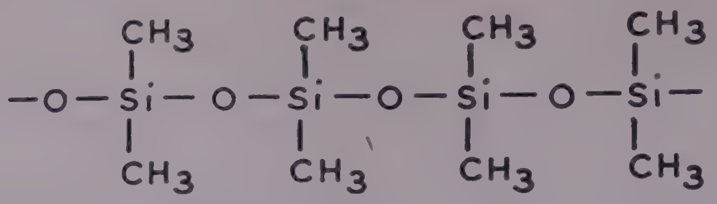


FIGURE 1

Relationship between percentage of rings formed and number of carbon atoms

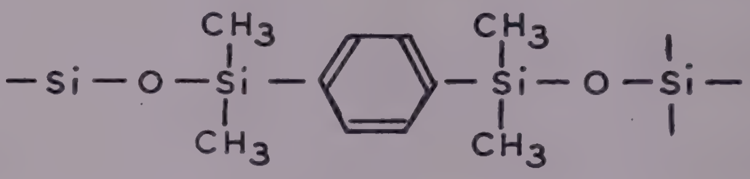
as a by-product. If four or seven carbon atom rings are formed, then we get about 15 per cent of the polymer. But eight or more membered rings are formed only with difficulty so that we are able to get long polymer chains and not rings with monomers each having four carbon atoms or more. The reaction is relatively easy to control and mathematical relations for the rate of the reaction and molecular weight of the polymer, i. e. the average molecular weight, has been proposed. Mostly, the polyester preparation is conducted as a continuous process- not as a batch process- and from the amount of water that has separated, one determines the number of ester bonds that have been formed, in other words, the conversion to high molecular weight product. In the continuous process, starting with ethylene glycol, the polymer molecules as they are formed, are removed up over a heated screw where the polymerization continues to form bigger molecules and the water of condensation is removed continuously. The degree of polymerization is controlled by the speed of running the screw. This is purely an engineering device. The polyester melt goes directly for casting or spinning so that cooling and inhomogeneous remelting while processing later are avoided. Different types of monomeric units have been examined for polyester preparation but the best is 'polyethylene terephthalate', a fine macromolecule for fibres.

These are two-dimensional linear molecules but with controlled cross-linking of polymers, a network with good high temperature resistance is obtained. For such types of heat resistant materials, silicones have been tried.

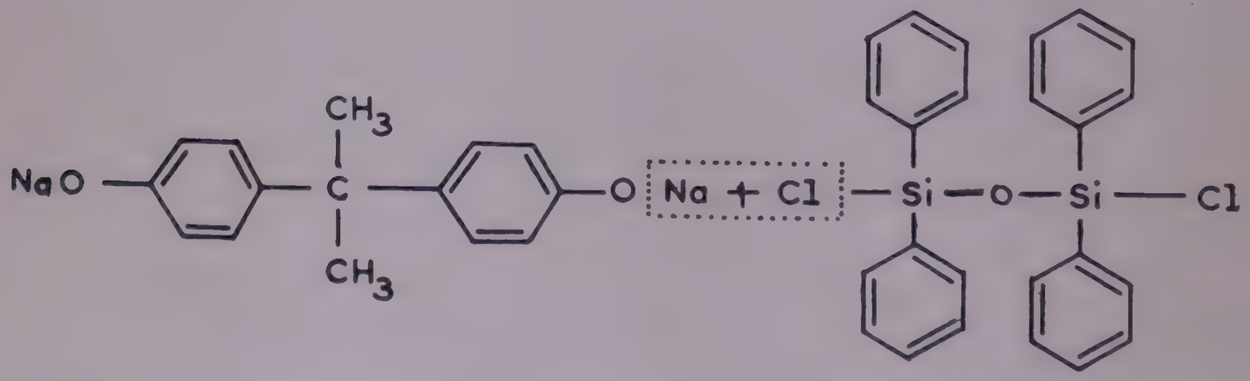


$$-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-$$

But these form rings about 400°C. splitting off short fragments. Introduction of an aromatic ring in the chain as in the following representation reduces ring formation:



There is another polymer, a sort of hybrid between silicone and Terylene that shows excellent rigidity and better temperature resistance and also does not form rings because of the presence of the phenylene group in between silicone segments. Such a polymer can be prepared by reaction of the following sodium phenolate obtained by condensation of acetone and phenol with a chlorosiloxane, e. g.



Similarly bisphenol is reacted with phosgene to yield polycarbonates. These are some excellent heat stabilising building stones in polycondensation reactions.

Another kind of polymer with very interesting properties is the block polymer. In a conventional copolymer, the molecules of the individual monomers (E & P) are introduced at random and the different monomeric units are blended intimately on a molecular scale. But if a long segment of a polymer E_n is joined to another long segment of a different polymer P_n, we get a 'block' compolymer

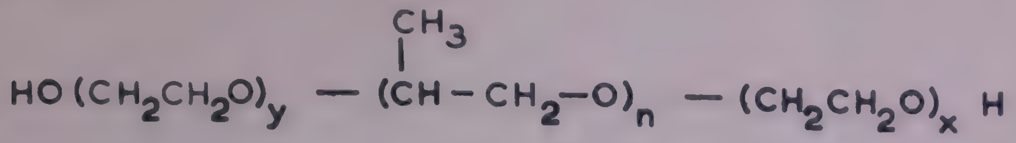
---- EPEPEPPPEEPEPPEEEP ----

Random copolymer

-- EEEEEEEPPPPPPPPPEEEE--

Block copolymer

Block copolymers have a number of useful applications since the different polymer chains retain their individual properties in the block copolymer also. For example, one can combine a water soluble polymer with a water insoluble counterpart to form a block polymer which acts as a surface active agent. Such block copolymers of ethylene oxide and propylene oxide are marketed under the trade name, PLURONICS in which the ethylene oxide chain is the water soluble part.



$$HO(CH_2CH_2O)_y - (\overset{CH_3}{\overset{|}{C}}H - CH_2-O)_n - (CH_2CH_2O)_x\ H$$

Pluronics: In conventional detergents, the surface activity depends on micelle formation which once again is dependent on temperature and concentration of the detergent molecules. But dispersions formed with block copolymers have very high stability virtually independent of temperature. Their total molecular weights are in the range of 10, 000 to 50, 000.

Sometimes it is desirable to have elastic fibres which are also strong and it is possible to prepare such a product by formation of a block copolymer of an elastic polymer with a rigid crystalline polymer. The elastic part is made for example, by condensation of adipic acid with excess of ethylene or propylene glycol, so that hydroxyl end groups with a molecular weight of about 3000 are got., The crystalline fibrous part is synthesised as usual from terephthalic acid and ethylene glycol, once again with hydroxyl end groups, having molecular weight in the range of about 15, 000. Now if those two blocks can be united, the fibrous and the elastic segments, to form a block copolymer, then we get the desired material, the elastic fibre. An excellent reagent to combine these blocks into a still higher polymer is a di-isocyanate, say toluene di-isocyanate because the isocyanate groups react readily with the hydroxyl end groups of the polymers to yield a block copolymer in which are incorporated amorphous, elastic as well as crystalline fibrous segments as shown in Fig 2.

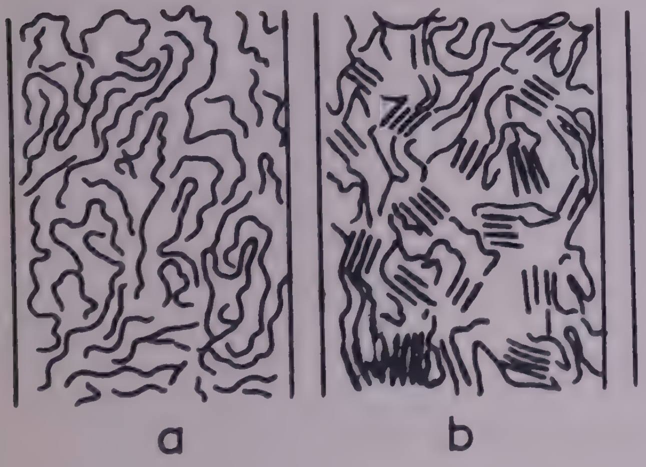
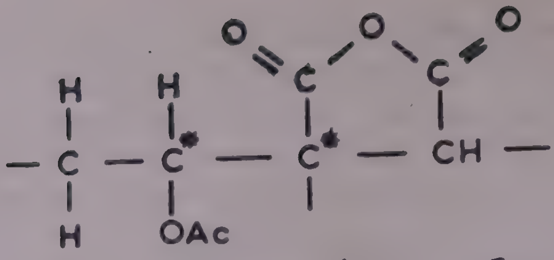


FIGURE 2

Structure of polymers:
(a) amorphous; (b) crystalline

This is molecular engineering to achieve the desired end and represents the typical modern approach in building molecules of definite structures to incorporate specific properties in the field of rubbers, fibres and plastics.

Another interesting example of current progress in the synthesis of polymers is the synthesis of optically active macromolecules. Let us take the copolymerization of vinyl acetate with maleic anhydride. If we consider the copolymer unit represented here, we find that the successive asymmetric



(ld, ll, dl, dd)

carbon atoms marked with asterisk can have any of the configurations 'd' or 'l' and any combinations of them, ld, ll , dl, dd. In fact, the polymer formed is not optically active because no particular conformation is favoured in the transition state of copolymer formation. On the other hand, if we take vinyl lactate, prepared from optically active lactic acid - say d-lactic acid, so that the ester group - the lactate group is optically active, and copolymerize this with maleic anhydride, some ordered addition in a preferred configuration seems to take place. If the ester group is hydrolysed off, we recover the d lactic acid, but the polymer residue also is optically active, which clearly shows that the copolymerization is stereoregulated apparently because of the optically active ester group in one of the monomers. If we filter dl strychnine, a racemate, through such a specimen, a separation occurs on the basis of the optical activity of this polymer membrane which we can call an exchange membrane. Obviously, this example illustrates another aspect of stereoregulation and the rather interesting properties and possible application of the obtically active polymeric products obtained.

DISCUSSION

14. Mr. A. Y. Kulkarni: Recently attempts are being made to form block copolymers of the already existing natural fibres like cellulose and wool with the addition or condensation polymers. What properties would the resultant graft exhibit? How could one detect a true graft from a physical deposit?

Prof. Mark: If one polymerizes acrylonitrile in the presence of cellulose for example, about 75% is grafted and 25% is the free homopolymer. The graft polymer would exhibit better resistance to moths and microbial action. One grafts nylon or wool to improve resistance to moisture. Homopolymers can be separated by solvent extraction from the true graft polymers.

15. Dr. P. K. Bhattacharyya: What about the N-carboxyanhydrides of amine acids? They are supposed to build themselves up on a helical structure.

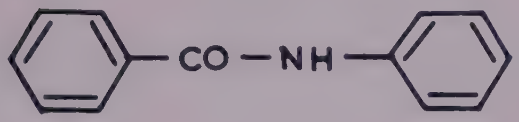
Prof. Mark: With these optically active monomers, optically active polymers are formed. Prof. Overberger has similarly worked with caprolactam.

16. **Dr. R. V. Subramanian:** We hear that a process based on telomerisation of ethylene to lead to amino enantic acid and Nylon-7 from it has been developed extensively in Russia. How do the product and the new process compare with the existing ones?

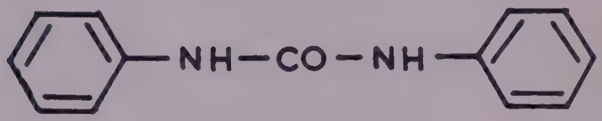
Prof. Mark: The amino enantic acid is made by telomerisation but the haloalkanes initially formed are mixtures of C_9, C_7, C_5, etc. which are difficult to separate. The recent work is mainly from the laboratory of Prof. Nesmyanov and his colleague Mrs. Freidlina who report about 65% yield of desired product. But the nylons obtained (Nylon 7, 9 etc.) are just as good as Nylon 66 probably, but not better.

17. **Dr. N. D. Ghatge:** Which of the following ring systems are more stable towards heat?

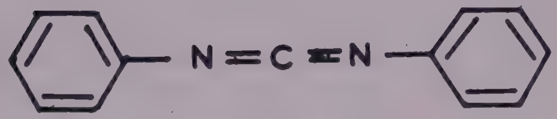
(a)



(b)



(c)



Prof. Mark: System (a) is more stable than system (b); (a) can stand up to 400-500°C. for two to three hours, whereas (b) can split off CO from the system. Polymers of type (c) have not yet been tried.

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FOUR

Characterisation of Polymers

We will discuss now the problems of the characterisation of large molecules. When we talked about characterising macromolecules ten years ago, we were mainly concerned about molecular weight, molecular weight distribution, end groups, and eventually branching. Those were the main problems to be tackled. Today we want much more. Today we want information concerning the microtacticity of the given material, i. e., the exact way in which the individual monomers are tied to each other sterically, so that there are only two types of experimental approaches in polymer characterisation, one of which is the classical approach, which is satisfied with the molecular weight averages, molecular weight distribution, with end groups and eventually branching, and the more modern approach which gives information concerning the exact isomeric character of the molecule under consideration. Let us go quickly through the first part and ask ourselves what progress has been made in the standard methods for the determination of the quantities mentioned? Taking first the number average molecular weight, not much substantial progress in the method of osmometry has been made. Some useful improvements, viz. small osmometer, micro-osmometer, more permeable membranes, less permeable membranes, thinner membranes, with which eventually osmotic equilibrium can be attained today within 20 minutes or so, membranes which can withstand a temperature of 150°C, have been made. But this is all really just standard improvement which has resulted in more handy and easier methods. The problem of molecular weight determination is always in the intermediate range say 2,000 below which standard methods such as vapour pressure, boiling point elevation and freezing point depression work satisfactorily and 10,000-15,000 above which the osmotic method starts to operate.

There has been some very interesting progress in this intermediate range, mainly through the use of very sensitive thermistors. You have a solution of a polymeric material in a cell and the pure solvent in another cell above so that the vapour of the solvent comes into contact with the polymer. You have a thermistor in each and both are then switched against each other, so that actually we have a bridge, and measure the temperature difference between those two surfaces. Now, since the vapour pressure of the solution is lower than that of the solvent, there is more condensation on the solution side than on the solvent side and the heat of condensation raises the temperature of the solvent and this temperature difference is actually measured. From this temperature difference, the difference in vapour pressure is computed by calibration and the molecular weight is obtained by the application of thermodynamics. This method works excellently over the whole range up to 35,000, so one can measure molecular weights of cellobiose, cellotriose, low molecular weight dextran and low molecular weight cellulose. This method when once it is worked out, is convenient and is practically automatic.

In the domain of end group determination, which is another way to measure the number average molecular weight, the problem is the other way round because it is very difficult if the molecular weight is very large. We have only a few end groups per gram and their determination is complicated and there, Professor Palit in Calcutta has developed a very nice method, viz. the dye distribution method, and this operates as follows. Suppose the end group is carboxyl or sulphonic acid group, then what one does is to dissolve the polymer, say polystyrene made with a bisulphite accelerator in $CHCl_3$ or CCl_4, to get of course a colourless solution and pour above this a very dilute solution of methylene blue in water. Now, no methylene blue whatsoever migrates into the CCl_4 phase as can be seen by shaking and letting stand when the dye solution will be blue and the CCl_4 layer will be completely colourless. But, if at this stage, a very small quantity of sulphuric acid is added then of course the sulphuric acid combines with the methylene blue to form a salt and the blue colour is acquired by the CCl_4 layer. What sulphuric acid does, is also what the SO_3H end group does in a polystyrene molecule and if we have the chloroform or CCl_4 containing a polystyrene, which has SO_3H end groups, then migration of the dye takes place into the CCl_4 phase which gets coloured. The intensity of the colour can be measured colorimetrically and a quantitative determination of the concentration of these end groups even up to 10^{-6} can be made. It is one of those very sensitive colour spot tests translated into application in solution. So the colour distribution or colour partition technique for determination of end groups is a very interesting method to find the number of average molecular weight of materials which have a high molecular weight where osmotic method does not work any more.

Now, coming to the weight average molecular weight, a classical method for determining weight average is light scattering. The light scattering method has also been improved in many respects. Sensitivity has been increased and all operations have been improved. The main worry in carrying out the light scattering measurements is the purity of the solution. Any dust in it or something else which causes a lot of turbidity should not be present in the system. So, automatic types of filtrations and centrifugations have been worked out and the light scattering equipments themselves have been improved, but there has not been any fundamental addition to the method since Zimm's classical work. This is very popular and reliable. Of course from the dissymmetry, we get the dimension of the macromolecules and eventually we get quite a good deal of information about branching and from the intensity itself we get essentially the weight average.

The other method which is important for determination of weight average is the ultracentrifuge method. One improvement has been added to our oscillograph instruments in the last few years. The principles of the method are very well known. Let us say we have a solution of polystyrene in toluene, and at the beginning, the solution is completely homogeneous. Now we apply a gravitational force and the large molecules slowly settle down in the sense that the concentration down at the bottom becomes larger than up at the top and if we then measure the concentration profile from the bottom to the top, we get a clear set of curves [Fig. 3]. Then as the sedimentation proceeds, the concentration is more at the bottom and less at the top and we get a family of curves after a few minutes and finally most of the material is compressed at the bottom [Fig. 3]. Long ago Svedberg and his associates had developed a theory of this process, which is essentially a superimposition of diffusion

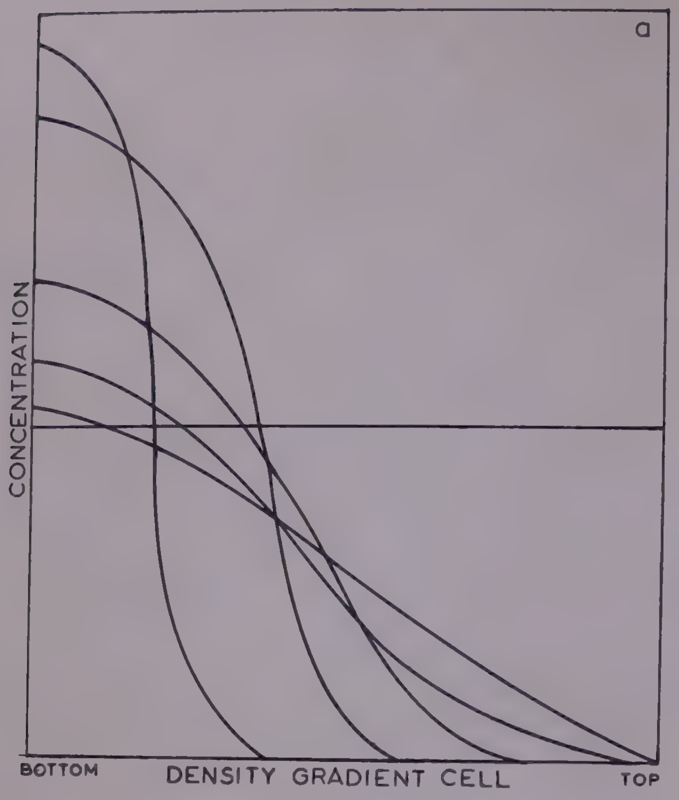


FIGURE 3

Variation in concentration with gravitational force for a polymer solution

and of sedimentation in the sense that the gravitational force pushes the material down and as soon as a concentration gradient develops as a consequence of this, the diffusion pushes the molecules back again. And, then we use a little bit of mathematics in terms of the partial differential equation, which describes the counteraction of these two phenomena, one of them hydrodynamic, the other one thermodynamic i. e. statistical. Every differential equation needs a boundary condition in order to arrive at a concrete solution and that is where the trouble starts, because we do not know exactly what is the boundary condition at the bottom. We do not know if the macromolecule comes down and sits down at the bottom, or if it is immediately reflected, or whether it moves around at the bottom; so the exact description of the phenomena at the bottom of the cell is impossible. Then one has always made certain assumptions which probably are quite reasonable. If one wants to evaluate the equations with great precision, then one cannot rely on these assumptions. Evidently, it would be the best if the bottom of the cell, i. e., the place where the polymer accumulates, would be in the middle of the cell. And this is precisely what one can achieve. A solution of polystyrene in carbon tetrachloride or chloroform of a certain concentration, say 0. 05 per cent, is taken in the cell, and the same polystyrene dissolved in toluene to give the same concentration is added on top of it. Then the two liquids are completely mixed. This is the very classical method of a density gradient tube. The density gradient which increases from the specific gravity of toluene (0. 8) to specific gravity of carbon tetrachloride (1. 6) is remarkably linear [Fig. 4]. At the bottom and top of the tube, there are certain deviations but otherwise in the middle comes a linear plot. It can be seen that

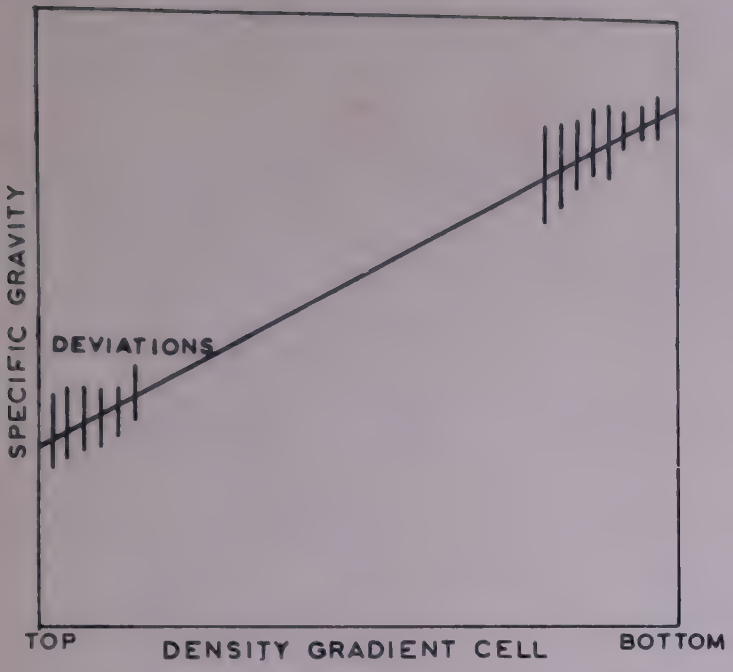


FIGURE 4

Relationship between specific gravity and height of density gradient cell

if we spin this density gradient cell, the polymer will neither accumulate at the top nor at the bottom, for it accumulates at the point of the specific gravity of the polystyrene, viz. 1.18. In other words, the accumulation takes place in the middle and if we translate this into a curve, we arrive at the following situation [Fig. 5]. As we spin around for a while, we get a maximum and the important

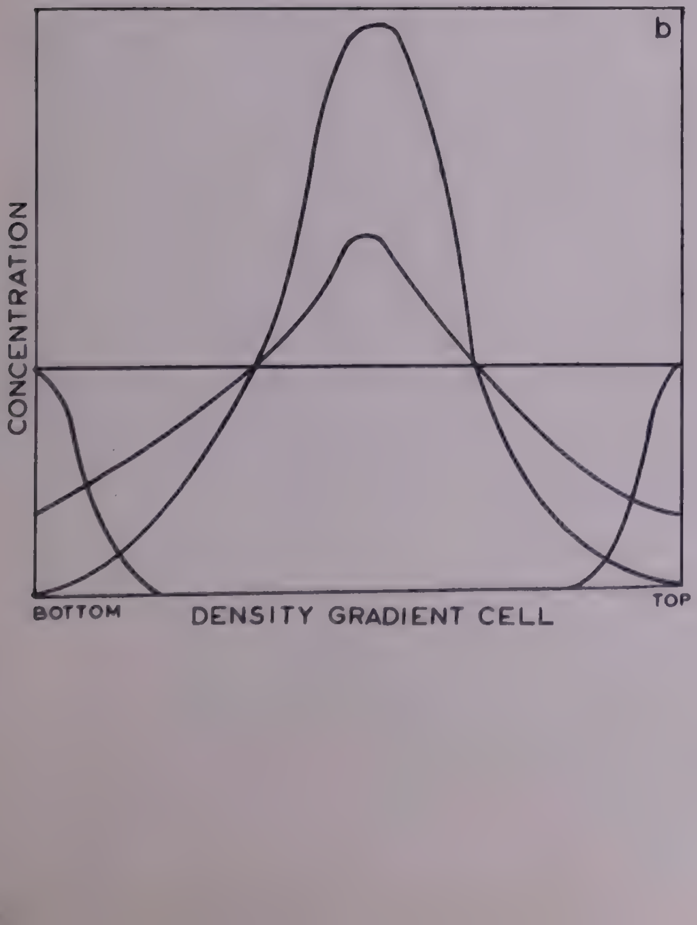


FIGURE 5

Variation in concentration with gravitational force for a polystyrene solution part of the curve is at the middle of the cell and there is no question about boundary conditions. We do not really care what happens at the real top and the real bottom. Now, the analysis of this problem by a number of people, particularly Williams in Wisconsin, has shown that each one has a characteristic shape and if one has a precise picture of this graph, one can determine all the three average molecular weights i. e. the number average, weight average and the Z-average. Well, we really know that this graph has a great precision and by the application of the density gradient method, one can get this with the required accuracy so that actually from sedimentation velocity measurements one can get all the three averages. This method is also extremely valuable for the molecular weight distribution because evidently the shape of this graph reflects the molecular weight distribution and very small impurities of a higher or a lower molecular weight can be ascertained by virtue of the fact that this graph assumes a different kind of shape and it is thus an improvement of the ultracentrifuge method.

The most effective application of this method actually has been carried out in the field of protein research. When the polymer is in solution we can investigate the molecular weight as such separate from the influence of other macromolecules. The polymers must be obtained in high purity, because impurities cause a great deal of disturbances and there are also sometimes practical difficulties. Supposing in a factory which spins polyacrylonitrile in 25 per cent solution, it is required to find the molecular weight of the polymer produced, then it would be necessary to know what is going on at the concentration at which the material is used. And the same thing is true when one spins polypropylene from the melt. So, when working with a melt and concentrated solution a rather interesting approach has been made in order to get the information from these types of systems. The procedure adopted is to take up the solution or the melt and measure the rate of flow through a capillary, as a function of pressure. Up to a certain pressure, nothing comes out of the capillary because the system possesses a certain elasticity and small pressures are just taken care of elastically so that there exists a certain critical point after which the curve goes up [Fig. 6]. Evidently, due to increase of pressure, the material becomes more and more fluid. The tangent of the graph is the fluidity. So, for a while the melt or solution becomes more and more fluid under the influence of increasing shear and that means physically that something is broken up, something is milled down into smaller moving volumes and sure

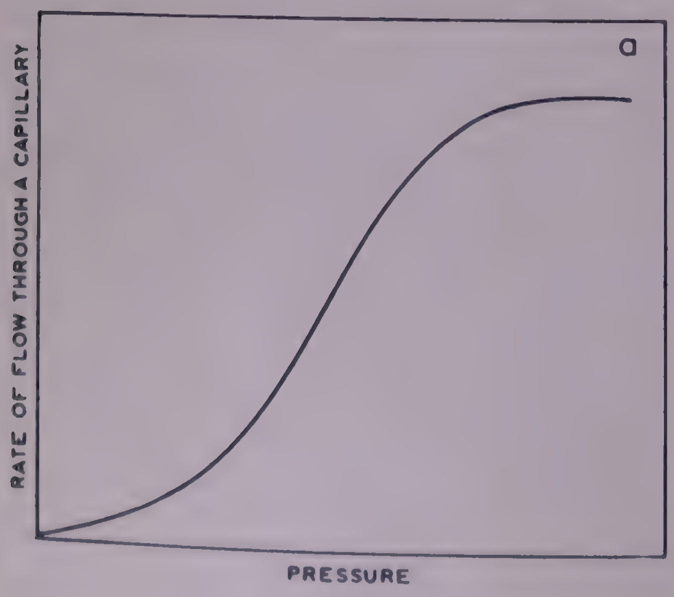


FIGURE 6

Relationship between rate of flow through a capillary and liquid pressure enough as the shear gets stronger and stronger, smaller volume elements will tumble along each other like ball bearings and cause the flow, but there is of course a point where the curve changes; there is an inflexion point; there comes a point of steepest slope, highest fluidity, lowest viscosity and that means evidently that at that point by the shear, which that pressure causes, the system has been milled down to the smallest possible moving volumes and evidently the smallest possible moving volumes are the molecules. So at this inflexion point the molecules themselves tumble along each other like tumbling wheels, like balls when they move, and from then on what happens is that the spherical molecules are deformed by the increasing shear and instead of having spheres moving, we have ellipsoids moving at higher and higher axis ratio and that of course causes an increase of viscosity and decrease in fluidity. The experimental proof or the justification for this interpretation is based on the appearance of flow birefringence which means there is orientation. Now a quantitative correlation of the pressure at which the steepest slope occurs with the molecular weight has been done mainly by Prof. Bueche at the University of Pittsburgh and by Dr. Edelmann in Berlin and several other specialists in the computation of such complicated hydrodynamic problems. Dr. Simha has done it and it is only necessary to get the polymer powder, and put it into the hopper of an extruder, turn on the pressure and heat and extrude to the inflexion point and then use the equation to find the molecular weight of the polymer. This method involves only 5-10 minutes, and the same can be used with a concentrated spinning solution of cellulose acetate, nylon or viscose or rayon. There is no complication in applying the method to get the molecular weight. This is a very valuable thing.

In order to fortify the theoretical aspects, Edelmann has taken polystyrene, fractionated it and then worked out its case for 6-8 fractions for which the molecular weight was known and then evidently he obtained a family of curves [Fig. 7]. Now, if the points of steepest slopes are taken and combined with each other, one arrives at a straight line which is parallel to the pressure axis. This is of course a phenomenon which has greatly helped the theoretical

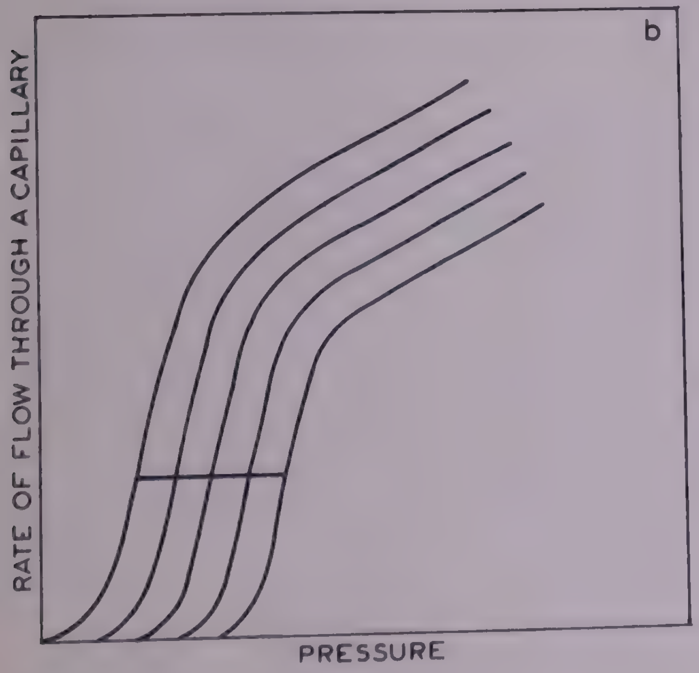


FIGURE 7

Relationship between rate of flow through a capillary and pressure for polystyrene fractions evaluation of the whole system because evidently it means that these curves really have the sense which has been ascribed to them. If there is no fraction but a mixture of two fractions, then one part will have its inflexion point at one pressure and the other part will have it at another pressure, so that for a very sharp fraction, the inflexion point, will be sharp; but in a mixture of many fractions or in a material which has a wider molecular weight distribution, a wider inflexion point is got. In other words, there is a certain linear portion; as indicated in the curve [Fig. 8] which is directly the integral molecular

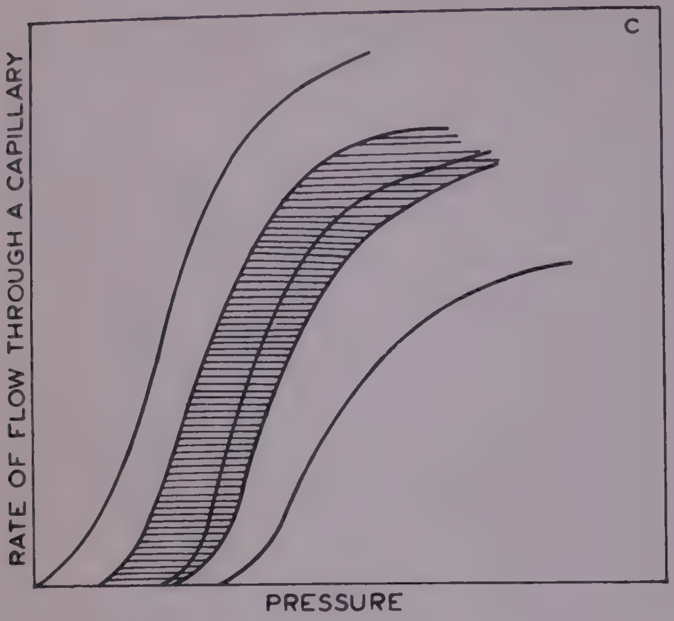


FIGURE 8

Relationship between rate of flow through a capillary and pressure for polystyrene mixed fractions

weight distribution curve . So directly from this measurement, the integral molecular weight distribution curve is obtained which means a wonderful product control method, rapid, reliable and very simple, which works for both concentrated solutions and also for polymer melts. This is not a method to determine exact molecular weight but it gives a fair idea of the order of magnitude. The same method gives very interesting information about branching. Prof. Edelmann who has particularly studied this procedure has found that for linear polystyrene fractions, the curves are characterised by the fact that the inflexion points are all on a straight line parallel to the abscissae. Polystyrenes which are branched can be prepared by grafting methods and the branching established by the Zimm Stockmayer and light scattering methods. Then for these fractions he found that the inflexion points were on a straight line again but the straight line was inclined against the axis [Fig. 9]. Prof. Edelmann has correlated this inclination with the degree of branching and purity so that one might even have a simple method for the determination of the degree of branching of vinyl type addition polymers. Considering the other question namely, what do we do if we want to determine the degree of tacticity of a linear vinyl type macro-molecule quantitatively, Prof. Natta has found that this can be done by the use of X-ray diagrams. Both isotactic and syndiotactic polymers give very good X-ray diagrams which are different from each other. This X-ray method tells us about an isotactic or a syndiotactic material down to about 85 per cent isotacticity or syndiotacticity;

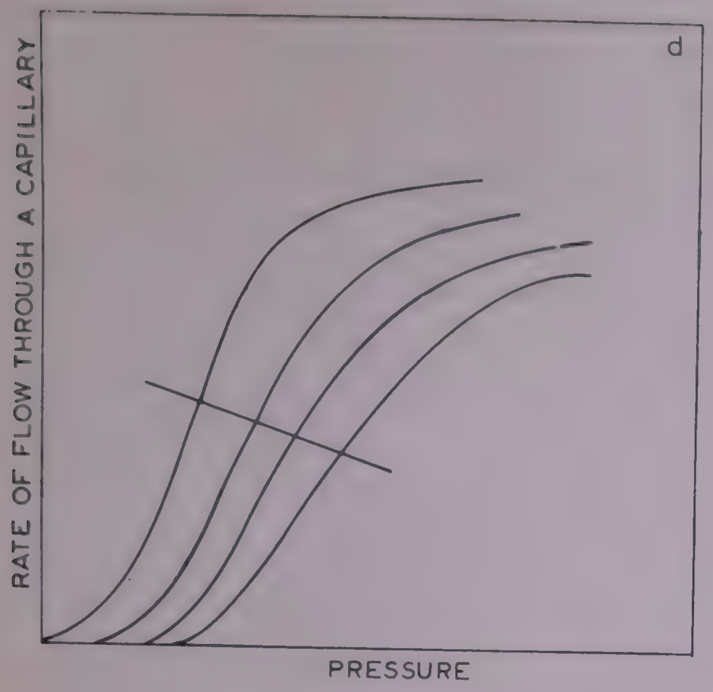


FIGURE 9

Relationship between rate of flow through a capillary and pressure for polystyrene branched fractions

in other words, it gives us 15 per cent on each side. Within this 15 per cent, from the quality of the X-ray diagrams, its intensity, sharpness of the lines, etc. we can qualitatively characterise whether a polymer is 90-95 per cent or 95-85 per cent isotactic or syndiotactic.

But about the intermediate range the X-ray method does not tell us anything at all. It is just an amorphous diagram; one might find faint traces of oriented interference spots as one approaches extremes of isotactic or syndiotactic but certainly in between there is nothing. Nevertheless, the properties still change quite a bit. The completely atactic material is quite soft and rubbery and it is rather hard and high melting as one approaches 100 per cent tacticity and it would be desirable to have a method which goes all across the whole range. One of the easiest methods which may be applicable is the following: Whenever the stereoregulated polymer contains a reactive group, for example, a carboxyl, hydroxyl or an amino group or anything of that kind, we can determine the degree of tacticity all across from highly syndiotactic to highly isotactic. This was developed in Brooklyn Polytechnic by Prof. Morawetz. In general, if we consider the macro-molecule in a very dilute solution, then we know the isolated macromolecule is a random coil. If there is no shear, if there is no force on it, there is no reason why it should not be a sphere and it is a sphere where the segments are densest in the middle and where they become less dense at the surface and the density profile which is a Gaussian curve is random. But it is only random, if we look at it from far away. If we look at a big tree from far away, we will say the branches are random, the leaves are random. But when we go nearer and nearer, closer and closer, then we will see that the leaves are sticking out in one definite direction according to a very definite pattern. As far as the micro-structure goes, there is no randomness for there must be no randomness; so if we now take one of these segments, it will possess a certain conformational regularity and as a consequence a certain shape. So, if we have five monomers, it is possible that this segment is completely isotactic. All the substituents are on the same side, or it is possible that it is completely syndiotactic or it is anything in between. Now let us assume that we have a highly, completely isotactic segment, an ester group such as in polymethyl methacrylate, then we have five ester groups attached to the segment in the isotactic location. Now we react this system with a base to hydrolyse the ester. Then because of the proximity and because of the special position of the ester groups in respect to each other, we would get a characteristic rate of hydrolysis, because it is well known in organic chemistry since many years that the rate at which oxalic ester hydrolyses is quite different from the rate at which malonic ester hydrolyses, in other words, the distance between the hydrolysing ester groups plays a big role in respect to the absolute value of the rate constant. Now Prof. Morawetz made a highly isotactic polymethyl acrylate and also a highly syndiotactic polymethylacrylate using the methods which were well worked out by Prof. Fox and his colleagues in the laboratories of Rohm & Hass. On measuring the initial rate constant of hydrolysis, he found a certain value for the highly isotactic and a different value for the highly syndiotactic material. Then he took one or two materials which were not quite so highly stereoregulated - then he combined the values by a line which is not a straight line but with a little bit of a curvature and this line now is a calibration curve [Fig. 10]. Now with an unknown polymethyl methacrylate or polymethylacrylate or polyvinyl acetate or any polymer which has the possibility of being hydrolysed, it is possible to determine the rate constant and using the calibration curve the percentage tacticity can be found. This is a chemical method which determines the detailed environmental conditions in the neighbourhood of a certain monomer by virtue of a rate measurement. It is also a very simple method because it is only necessary to carry out the hydrolysis of an ester. But the trouble is that it works only on materials which have such reactive groups. In other words, its practical application is limited to acrylic acid derivatives and vinyl alcohol derivatives and also, may be, vinyl amine derivatives but for isotactic or syndiotactic polypropylene, polystyrene or polyvinyl chloride we cannot apply this method.

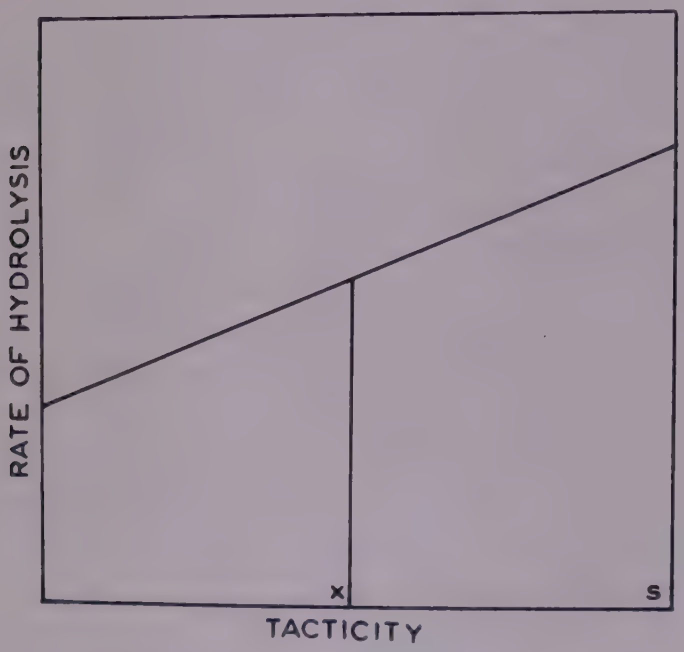
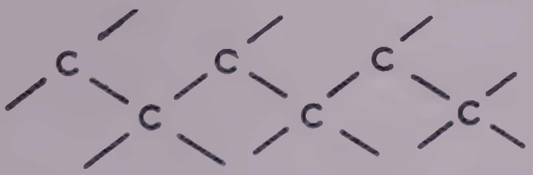


FIGURE 10

Relationship between rate of hydrolysis and tacticity of a polyester

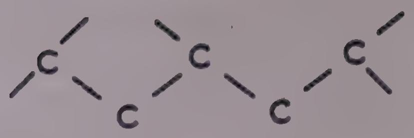
Now another method which unfortunately also relies on the reactivity but which is able to confirm the results from this method has also been worked out at the Brooklyn Polytechnic by Prof. Goodman. It depends on optical activity. It is well known that if an ester of oxalic acid is prepared with an optically active alcohol like terpeneol, we get a certain activity. Now if the malonic acid ester is prepared with the same alcohol, the activity is quite different because the two asymmetric centres are at a different distance from each other and they cooperate in terms of producing this circular birefringence. The closer they are, the more effective they are. The farther they are apart, the more each works for itself. In the adipic acid ester it is practically the additive contribution of terpeneol, d or l, but in the case of oxalic acid ester there is an additional synergistic effect and this evidently also can be used to distinguish between highly isotactic and highly syndiotactic because in the isotactic case the optically active alcohol residues are closer together than in the syndiotactic. So we have the same general phenomenon, viz. environmental influence on the optical activity, and with its aid, it is possible to determine the exact position of the active groups which in this case again has somehow got to be connected with a carboxyl group or hydroxyl group or amino group. Whenever we have a polymeric material which has such groups, there is no difficulty or there is no problem. But with polypropylene, polystyrene or any other polymeric material which is stereoregulated and which has no chemical reactivity, it seems that the only promising method is NMR. It will be nice if one could get the information about this intermediate range from infra-red absorption spectra but this method does not really tell us exactly what we want to know. What the infra-red method measures is the vibration of atoms against each other, eventually, torsional vibrations, more complicated vibrations of chain segments and these do not depend very sharply on conformational and configurational conditions. There have been a few cases where one can make statements whether a polymer is in a highly isotactic or syndiotactic range. Infra-red absorption spectrum of highly isotactic polypropylene is quite different from the other which is highly syndiotactic. But this method is not needed in this case because of the applicability of the X-ray method. But in between, one really finds difficulty. Dr. Bovey in the United States has started a systematic investigation of the application of the NMR method to this problem as well as other such problems. It looks right now that it might be a pretty good method and the idea again is that whereas the macromolecule as a whole is random, if we go to localised conditions, we will have definite positions of all the individual atoms of the macromolecule. Consider the case I of a polypropylene segment with 3 monomer units.



I

(lll or ddd)

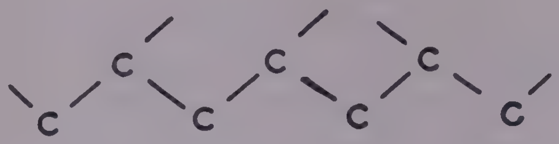
It can be seen that this can be contained in a small sphere with 3 Å radius and inside this sphere the protons, hydrogen nuclei are all arranged according to a certain fashion which depends on the steric character of the three monomers. Evidently, the nuclear magnetic response of this monomer will depend on both of its neighbours. So we have to always look at three monomers. Focussing our attention on one in the middle it will be clear that its response, its absorption line or its contribution to the total absorption in the NMR experiment will be influenced by both neighbours. If both neighbours have the same configuration, i. e. all three are lll or ddd we have an isotactic triade. If both neighbours have the opposite, then we have a syndiotactic triade, and the middle monomer has a different configuration - II



II

(dld or ldl)

from the others and therefore inside of this sphere again the position of the methyl groups and H atoms will be different; here we have ldl, or dld. Evidently isotactic and syndiotactic are not enough. In order to complete this analysis there is a third possibility, i.e. on one side, the middle monomer has the same configuration-III but on the other side, it has opposite configuration. It will be ddl or lld and this also needs a name and Bovey has called it 'Heterotactic'. So in an isotactic triade, there is a



III

(ddl or lld)

certain response from the middle monomer and in the syndiotactic triade, there is another one and in a heterotactic triade, we have a response in between. This is exactly what one finds by experiment. Highly isotactic material has a sharp absorption at a certain point in the spectrum. The highly syndiotactic material gives a sharp absorption at a different point. Now looking at something which is intermediate, we will find the contribution of the isotactic triades, the syndiotactic triades and the heterotactic triades clearly differentiated from each other. This gives a complete quantitative analysis of the details of the sequence structure. Imagining a certain sequence it is possible to characterise it as follows: Assuming the sequence - lld, dld, lld, ddl, dll, the triades can be characterised as indicated in Table 1 -

Table - 1 Characterisation of Triades

Triade	Tacticity	Sequence
First	Heterotactic	lld
Second	"	ldd
Third	"	ddl
Fourth	Syndiotactic	dld
Fifth	"	ldl
Sixth	Heterotactic	dll
Seventh	"	lld
Eighth	"	ldd
Ninth	Isotactic	ddd
Tenth	Heterotactic	ddl
Eleventh	Syndiotactic	dld
Twelfth	"	ldl
Thirteenth	Heterotactic	dll

In other words, there are 13 ways in which this can be cut in triades. Of the total thirteen, eight are heterotactic, four are syndiotactic and one is isotactic, i.e. it will be 7 per cent isotactic, 28 per cent syndiotactic and the rest heterotactic. In this way, we get a complete quantitative description of the actual sequence of arrangement in a stereoregulated polymer. This can, however, be shuffled around, and completely isotactic. If all 'l' are together and all 'd' similarly grouped together, almost everything will be isotactic excepting two in the middle shown below and these two will be heterotactics.

(llllldlldddddd)
(llllllddlddddd)

Hence it is the shuffling, it is the detailed arrangement, it is the microtacticity which causes it. The aim is to analyse the macromolecules quantitatively in respect of the way in which the different configurations of the monomers are arranged along the length of the chain. By measuring the three intensities experimentally, the exact information needed is obtained which enables us to state that 70 per cent is isotactic and 20 per cent heterotactic and the rest syndiotactic. However, the trouble is that though it is almost ideal from the point of view of the result, yet it is not an easy experiment. First of all, a normal standard equipment for the NMR analysis with a high resolution power is needed. But unfortunately some materials do not give very true response. Excellent intensities and excellent responses are obtained from the method of NMR in the case of polymethyl methacrylate. Where this method is not needed, we can use the Morawetz method.

These are the presently available experimental methods for the determination of the microstructure of a macromolecule which has the possibility of being stereoregulated. X-rays are fine if the degree of regularity is high and if we want to penetrate into the domain of intermediate stereoregulation, we have at our disposal the methods of Morawetz kinetic measurements, optical activity, NMR, etc. There are just a few other methods which give approximate information about tacticity, like solubility, density. These give us an idea but are not absolute in the sense that they do not give the quantitative information that is needed.

DISCUSSION -

18. Dr. G. Narsimhan:	The quantitative characterisation of the stereospecificity of the polymer by the chemical reactivity of the system involves the measurement of the reaction rate constant which is a statistical characteristic and as such one can visualise the attack of the polymeric molecule by the diffusion of the reactant species, say, hydroxyl ions trying to penetrate the polymer network if the reaction rate is fairly fast.
Prof. Mark:	It is not fast, it is not diffusion controlled. But one has to use an alcohol where the rate of hydrolysis is slow so that one actually measures the rate of hydrolysis and not the rate of diffusion.
Dr. G. Narsimhan:	So the stress - strain diagram will not give any information about the stereoregulation of the polymer?
Prof. Mark:	That is right.

19. Dr. M. L. Lakhanpal: Referring to vapour pressure method for determination of molecular weights, naturally there is a difficulty in the accurate measurement of vapour pressure. But there is one differential manometer devised by Dr. Puddington. We are making use of it.

Prof. Mark: That is a method worked out by Dr. Puddington of National Research Council, Canada. He succeeded in getting molecular weight of 35,000 or so.

Dr. Lakhanpal: He has gone to 1,00,000.

Prof. Mark: Well, the trouble with the method is, it is very delicate. It is a very nice method; it is a direct measurement of vapour pressure difference with a glass membrane and it is just a manometric method. Well, I am sure if one has such an instrument working, it will be nice.

20. Dr. M. S. N. Rao: For constructing the molecular weight distribution curve, various average molecular weights are determined and then assuming a reasonable form of distribution function the curve is constructed. It happens often that several distribution curves can satisfy the various average molecular weights. I wonder if there is an absolute way of getting the curve from molecular weight data alone.

Prof. Mark: No. I think the three averages just give you an approximate idea about the polymolecularity; what the actual shape of the distribution curve is, they do not tell you.

21. Mr. A. Y. Kulkarni: Can the saponification of polyacrylonitrile to polyacrylic acid with alkali be used for estimation of the polymer content in a cellulose fabric?

Prof. Mark: Yes. This is of course not a precision method. We have yet to calibrate with pure polyacrylonitrile under the same conditions and find whatever is not hydrolysed and then you just determine the - COOH groups. Probably the best way is the dye distribution test of Palit because this is a very good test for the determination of - COOH groups.

Mr. A. Y. Kulkarni: But polyacrylic acid would be water soluble.

Prof. Mark: Yes, but you can keep it in an environment in which it is not soluble - one must not take it in water, acetone, etc.

22. Mr. Kulkarni: What initiations are best for grafting of polyacrylonitrile on cotton fabrics?

Prof. Mark: The best grafting initiator is ceric ion. That is the best. Ceric ion forms a complex with cellulose and therefore the initiating free radical is actually at the chain. This gives a very high grafting efficiency and that has been described in detail in a number of papers by Immergut.

23. Mr. R.K. Marphatia: Regarding the method of determination of acrylonitrile content of textile printing binder on a fabric, will not the use of strong reagents like 40% NaOH and potassium sulphite attack the fabric and thereby vitiate the result?

Prof. Mark: Well, it does not matter. You don't want to use the fabric after you have carried out the test and as long as you work in the absence of O_2, I don't think that any -COOH groups would be produced.

Mr. Marphatia: How is $K_2S_2O_8$ used as initiator for grafting?

Prof. Mark: Yes, if we have a fabric which is insoluble, take a sheet of cellophane, soak it in water which contains the $K_2S_2O_8$ and bisulfite and you add the acrylonitrile and you get the grafts. Then you will have the acrylonitrile grafted on the surface and you wash everything out - $K_2S_2O_8$ and bisulfite and then with this, you go through that procedure.

24. Mr. T.V. Subba Rao: I would like to explain the point raised by Dr. M.S.N. Rao. The difficulty in locating the peak is we have only these average molecular weights. How to know the range? How to know this range only from average? It is impossible to know the range if only the average is known because this curve can be defined if only you know two parameters. So the easiest way to get at this is if we can fractionate that material and get at least two molecular weight determinations and know the percentage of that fraction and the molecular weight of the fraction, then the whole curve is defined. We can calculate the standard deviation and from that we can put this curve. The molecular weight distribution curve is the normal curve which needs two parameters for characterisation, (i) average and (ii) standard deviation or range. The latter being approximately 3 standard deviations on either side of average. In order to know the standard deviation, the material may be separated into at least two fractions and from the proportion of the two fractions and the molecular weight of the fraction, the standard deviation and from that the range for the distribution of molecular weights can be calculated.

Prof. Mark: Talking about fractions, there are now available for distribution three fractions of polystyrene. They have been made by the living polymer method and they have been refractionated each of them, one has molecular weight of 60,000, the other one 120,000 and other 300,000. They are available with the International Union. Now these fractions are rather good and all three averages have been determined for them by a number of methods and actually for the middle fraction $\frac{Mw}{Mn} = 1.04$ and $\frac{M}{Mw} = 1.02$. So according to the average values, they are pretty good. With them now one can produce mixtures and with these mixtures one can appreciate the meaning of these values i. e. these three values if one does not know how the mixtures are made.

25. Mr. P. S. Sarfare: How good is the method of turbidimetric titration to determine the polydispersity of macromolecules?

Prof. Mark: Well, turbidimetric titration method is very good. Talking about molecular weight distribution, I did not mention it specifically because not very much new is there to report but two methods known already are really good. One is turbidimetric titration and other is that which Dr. Hicks has developed at the Farbewerke, Hoechst and that is to put a wire, powder or film in a large surface with a very thin form of the polymer and wash it off fractionally with solvents of increasing solution power. This is a kind of an automatic way of separating the polymer of a very thin form of different molecular weight species and other one is turbidimetric titration.

26. Mr. S. Gundiah: Prof. Umstatter's method used by Edelmann does not depend only on the inflexion point in the flow rate versus stress curve. It depends also on two other parameters. I think one of them is the variation of viscosity with temperature and another is the variation of viscosity with concentration.

Prof. Mark: Sure, but the special application which we have discussed, works with a given concentration and given temperature.

Mr. Gundiah: But the equation contains those two parameters also, viz. temperature and concentration.

Prof. Mark: But it will work at a given temperature. Either we want to study the entire phenomenon or we want to determine the molecular weight and if we want to study the entire phenomenon, you are quite right. It depends on a large number of variables. If you want to use this phenomenon for the determination of molecular weight, you keep the temperature and concentration constant and do that.

Mr. Gundiah: With the data obtained at one temperature and one concentration, can it be determined?

Prof. Mark: Sure,at any temperature and any concentration, you get the same value.

Mr. Gundiah: Prof. Edelmann's paper contains these two parameters.

Prof. Mark: Sure, it contains the parameters but we are not worried about the fact that it contains the parameters. The weight average molecular weight according to the situation is this: The Mw according to this equation Mw = f (PCT etc.) is a function of the pressure at which the steepest slope is reached. Concentration of solution, temperature, solvents and one or two others – I will keep all these constants. Besides when we work at such and such concentration and such and such temperature and such and such solvent, wherever we apply this to determine this P.

Mr. S. Gundiah: Such concentration is there in Prof. Umstatter's and Edelmann's papers.

Prof. Mark: Yes, this concentration in the method described is 25% and this concentration in the equation is very dilute for the other evaluation. But if one takes from the melt, then one does not worry about concentration at all.

27. Dr. P.K. Bhattacharyya: In random polymerisation, there are pretty large number of molecules produced. Now after you take NMR, you get overall picture of isotactic, syndiotactic triades. This is just a a statistical distribution. Is this kind of data reliable in the sense that they are reproducible? Say, if you polymerize propylene under one condition and you get the same distribution?

Prof. Mark: No, No. If you use certain specific condition, titanium trichloride, and aluminium isobutyl, so much in such and such solvent, etc. one gets pretty close to the same standard distribution, each time.

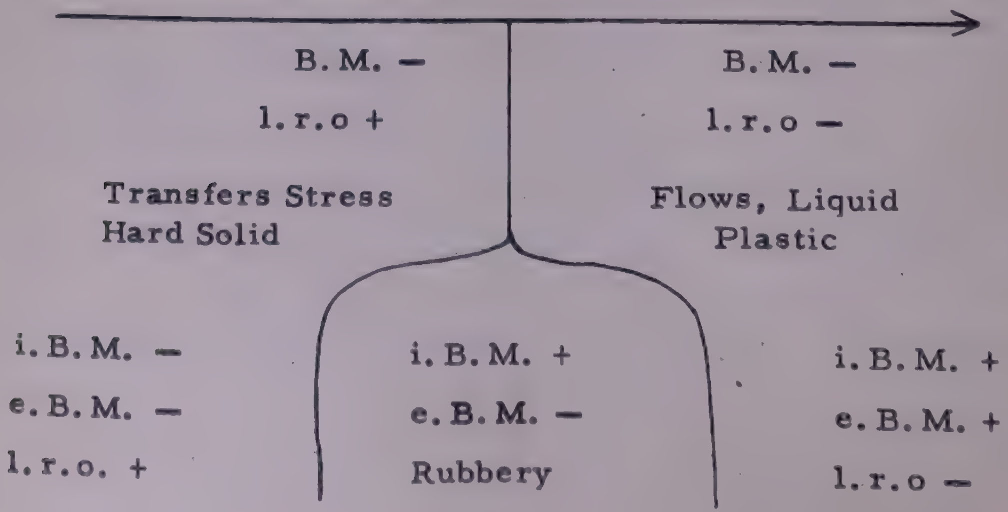
Dr. Bhattacharyya: But what happens when you polymerize by free radicals?

Prof. Mark: Then of course, you get something entirely different.

FIVE

Correlation Between Structure and Mechanical Properties of Polymers

In this lecture are discussed the essentially recent advances in the understanding and use of the polymeric materials concerning their mechanical properties, hardness, tensile strength, abrasion resistance, their solid state characteristics like softening or melting, and their solution properties such as solubility. In order to get a general classification and general understanding, there exists a very simple but quite useful approach. This consideration starts from a comparison of macromolecular materials and normal low molecular weight substances. The low molecular weight materials can be obtained in three states of aggregation, solid, liquid and gas. Polymeric materials are never in the gaseous state and all we are concerned with are condensed systems which are liquid or solid. Looking at a normal substance such as naphthalene, paraffin or any low molecular weight organic substance, it is known that it can exist as a solid or as a liquid. The conditions in which the material exists in each of these two cases, specifically in the case of a crystalline solid can be compared to that of an audience in an auditorium. Each individual molecule sits in a certain equilibrium position; it moves about a little in this position but does not move away, does not diffuse around. The essential characteristic of a crystalline



solid is that there is no molecular translational movement i. e. no 'Brownian movement'. As a consequence of that there is a sharp identity period, repeating itself many many hundreds, many many thousands, in fact many million times, inside the crystal; so we get a long range order (l, r. o). Now the next step is to ask ourselves what would be the response of the system of this kind to an external force? Evidently, because of the fact that every individual molecule is in a rigid situation and that the planes formed by these molecules are inflexible and rigid, a material of this kind, which we call a hard rigid solid, is capable of transferring stress.

So we have here a description of a low molecular weight crystalline material first in respect to the condition of the individual molecule, second in respect to the geometry of the phase and third, concerning the mechanical characteristics. How should we call that material? Now, let us assume that we increase its temperature, then eventually, as we put more and more kinetic energy into every degree of freedom, then the individual molecules start to vibrate more and more vigorously and eventually if the average energy of this motion has reached a sufficiently high value, the energy barriers between the individual equilibrium position will be separated. In other words, at a given temperature, the Brownian movement is activated and at temperatures higher than this critical temperature, the Brownian motion now is positive. As a consequence of this change, we can see that from now on there will be no long range order any more because of the randomness of the Brownian movement and if we take a material of this kind and subject it to shear, it will not transfer stress but it will yield and flow and this we call a liquid; so that actually there are two characteristic states, without Brownian movement and with Brownian movement; without long range order, with stress transfer as in a solid; with no long range order and with energy dissipation, we have a liquid and the temperature which separates these two types of materials is known as the melting point. Repeating the whole story for a macromolecular material, let us take up the case of polyethylene film or a nylon film, a rayon film which we draw and anneal repeatedly until it gives a very excellent X-ray diagram; and the fact that it gives a good X-ray diagram, shows that again there is no Brownian movement. Well, as a consequence, the X-ray diagram also tells us there is long range order because if there is no long range order, there is no diffraction of X-rays, there would be no obedience to Bragg's law and no sharp interference pattern will be seen. Also it is obvious that a rope of nylon, cotton or hemp transfers stress. When we increase the temperature, the characteristic difference is seen. If the temperature of a low molecular weight substance, say a crystal of sugar, naphthalene or paraffin is increased, then the molecules either move or they do not move. Suppose we have a very large chain, a large molecule of 1000 individual units long, then it is perfectly possible; in fact it is not only possible but we have to consider it as a fact that such a long chain may be in a state that in some parts there is already considerable internal motion whereas in other areas, there is relatively strong restriction. Any object which has many degrees of freedom can be partly activated. Moving one's fingers, and moving one's arms one can still remain in the same position. In other words, in the case of large molecules, particularly in the case of long flexible chains, we must consider the possibility that parts of the molecules already are carrying out motions but the other parts of the molecules are still restricted. The molecule as a whole does not move but the segments move. It is like taking a long snake and nailing it in the middle when it is going to move very violently; but it will not be possible for it to move away, as a whole. Now this indicates that in the case of a polymeric material, we really should distinguish between two types of Brownian movement, between an internal Brownian movement (i. B. M.) which reflects local mobility and an external Brownian movement (e. B. M.) which reflects the over-all displacement of the material and evidently as we increase the temperature, there would first be the internal Brownian movement activated and only later at a still higher temperature both the Brownian movements will be full of kinetic energy and will have to have here a + sign. So going to high temperatures, both the internal and external Brownian motions are activated and as a consequence there will be no long range order and there will be flow instead of stress transfer, and this will be a liquid; of course, it will be a very viscous liquid because of the size of the molecule but it will be a liquid. In other words, we have something which corresponds to the solid state of a low molecular weight material in such a temperature range where both Brownian motions are still frozen in and we have something which corresponds to the liquid in another temperature range where both Brownian motions are activated and this is a polymer melt. It has all the earmarks of the liquid, only difference eventually is that the viscosity is much higher and now comes the question, what is in between? This consideration has given us a new type of solid material; it has given us a new phase, because evidently, it is a temperature range in which both Brownian motions are frozen and if there is another temperature range in which Brownian motions are activated, there must be in between a temperature range within which the local mobility is already activated but the overall mobility is still forbidden. So by this consideration, we suddenly face the fact that a polymeric material can exist in three different states of matter, not in two. One corresponds to solid crystalline state, the other corresponds to the liquid- fluid state and what is the third? The third is the rubbery state. This combination of local motion and of overall rigidity is the characteristic for a rubber. In other words, the rubber state is really a combination between a solid and a liquid state. Rubber in fact is a liquid with a super-imposed system of fixed points or it is a solid with very accentuated local motion of the molecular segments. If a rubber band is pulled, then very small forces are sufficient to change the shape very considerably. Well, if it is so easy to change the shape, there must be something which helps in doing that and that is the + sign of the internal Brownian motion. In a piece of rubber, on looking into it, a multitude of long snakes which always move around may be seen. The molecules of this material - rubber - always move around like the molecules in a liquid but when this rubber is pulled more and more, after a while, it cannot be pulled any more without breaking it, and this means that the minus sign of the overall Brownian motion or external Brownian motion has been met when the rubber is let go and then there is a pretty quick return. It is a very drastic documentation of the fact that something in the sample moves rapidly, otherwise the sample cannot snap back the way it does. So, to be a hybrid between liquid and a solid is evidently the right characteristic for a rubbery material.

Now it can be seen from that actually, that conditions in the description of a polymeric material are somewhat more complicated than they are in a normal substance. We should not talk about the melting point of a polymeric material, because there is no melting point. The melting point, first order transition point, is characterised by the fact that in a simple low molecular weight substance, all motions are forbidden below this point and all motions are allowed above it. In the case of a plastic material we have two transition points of a different kind. We have a transition point in the low temperature usually called glass point or a brittle point, where one of the signs is changed viz. that referring to the internal Brownian motion but the other sign is still maintained. In other words, only half of the restrictions are lifted. Therefore, this is not a standard first order transition point but a second order transition point. Again, as we come to the temperature, where the other half of the restrictions are lifted, we come to the flow point or softening point and this again is a second order transition point. The fact that we talk sometimes about the melting point of nylon is caused by the accident that in the case of nylon and many other cases, these two temperatures are very close together. In other words, the range of rubberiness of nylon or polyethylene or many other polymers is very short. But if a nylon filament is taken and heated very very cautiously, then exactly somewhere about 248° or 249°, it becomes rubbery and then at 250°C. it melts. Usually one does not heat up the material so slowly and so carefully. But every polymer has two second order transition points which eventually are very close to each other and amount to more or less the melting point. If we increase the molecular weight of a material, it becomes more and more significant and necessary to talk about two Brownian motions. As long as the molecules are small, this has no sense. Either they move or they do not. In case of fatty acid chains containing 16, 18, 20, 22 carbon atoms, take for example stearic acid, it has a sharp melting point. But if we make a chain of 100 carbon atoms then gradually after a sharp normal melting point again the true second order transition point is obtained. Brownian movements develop gradually because of the necessity to take care of the existence of local mobility. The longer the molecules, the more clear-cut becomes this differentiation and for several substances phase diagrams have been developed and actually worked out. If the temperature is plotted against the degree of polymerization (DP) the curve appears as in Fig. 11

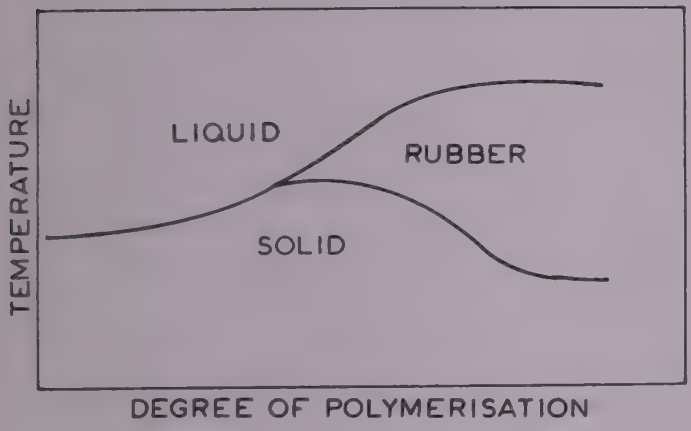


FIGURE 11

Degree of polymerization as a function of temperature describing liquid, rubber and solid phases

Styrene monomer has a certain melting point. The dimer, trimer, etc. have different melting points and as the chains are made longer and longer, the range of rubberiness develops and from a certain molecular weight it remains practically constant. Because it has a segmental characteristic, it does not depend on molecular weight as soon as we have reached a certain minimum molecular weight for its development. This has a practical application. Polyvinyl chloride, at sufficiently high temperatures is in the molten state and when a certain range of rubberiness is taken, say a few degrees, how can the range of rubberiness be widened? The first necessity would be to push the brittle point down as low as it can possibly be done and this is achieved usually by plasticisation. Either a plasticising monomer is added to form a copolymer or a liquid which is compatible with the polymer and softens it is added and then by favouring local motion we can go down to relatively low temperatures and still the local segmental motions will be functioning. But if we move internal

Brownian motion (+ iBM) to lower temperatures, we will also have to take a second step, as a consequence of which the onset of the external Brownian motion is moved to higher temperature and that, of course, is cross linking. So plasticisation and cross - linking together, widen the range of rubberiness. Plasticisation refers to the internal Brownian motion, to the local segment mobility; and cross - linking refers to the establishment of a system of fixed points which prevent the large molecules to slide along each other and which keep the negative sign of the external Brownian motion up to very high temperatures. This really is the essence of rubber technology.

All rubber technology is a combination of plasticisation and cross - linking. It is known that the calendering, milling and mastication of rubber is plasticisation and then of course the vulcanisation is cross-linking. Recently with many rubbers, even oil is added, real true low molecular weight plasticiser in large amounts 10, 20, 30, 40 per cent in order to get the low temperature behaviour of the material as good as possible and then this plasticised material is cross - linked. In this way we have materials based on natural rubber, or other hydrocarbon polymers where the rubber point may be at -60°C. and the flow point or the heat distortion point somewhere at 150°C. In other words, if we want, we can make the range of rubberiness to 200°C. wide or may be a little bit more. In fact with certain silicones and certain fluorinated elastomers, one can go down to -80°C. and up to + 180°C. so that in extreme cases, it is possible to separate these two transition points by about 250°C. Then within a range of 250°C. the material is a rubber.

In a fibre like nylon, of course, we will want to emphasise the solid state; we want to have as much of the material in the crystalline state; orient molecules and bind the molecules from the beginning so as to crystallise very efficiently. Then we would have both the Brownian motions frozen in; the material will be hard, strong, high melting, it will be resistant against swelling, and dissolution. In other words, it will have all the earmarks of the rigid phase. It is well known that the process of drawing off nylon imparts these characteristics to a nylon yarn. But taking undrawn nylon yarn which has some 60 individual filaments and drawing it quickly, the minus sign is hit. Now if drawn any more, it will break but now it is very strong. This gives a good X-ray pattern and this is now a material which by the process of drawing has been pushed down as far as possible into an area where both internal and external Brownian motions are frozen in at this temperature. If we heat it to 235°C, it will be a different thing. Now if you want a fibre, go down to the left i.e., rigid phase [Fig. 11]. If you want a rubber, stay in the middle. If you want a plastic, go over to the right, because there both iBM and eBM are allowed, that is, there we can form and freeze them down into the solid state. Hence the essence of this pattern is that any material which we make from a polymer actually contains all the three types to a certain percentage because whatever we do, spinning, milling, extruding, casting, we always start with the material either as a melt or as a solution because we need the two + signs (of Brownian motion) in order to give the material the desired shape. If we want fibre or film, again we need two + signs. Otherwise the thing is not going to flow. Now, then we get at the right shape and then we cool it down to room temperature or evaporate. We rigidify, and we freeze into the final object, a certain percentage of all the three states and how much of each of these three possible phases we do finally establish in a given material depends on us; it also depends on the rate of cooling, it depends on whether we orient when we cool or how fast we evaporate the solvent and so on, and this is the real essence of the enormous variability of polymer technology. Out of one and the same polymeric material;

out of one and the same kind of molecules, a whole spectrum of substances can be made depending upon what kind of ratio of those three phases are put into it.

This is a quite a familiar phenomena from metallurgy. In metallurgy, we do the same thing, we take iron and we add cobalt and we add carbon and then we heat to a temperature of 1700°C. and the whole thing is a liquid and at that temperature certain reactions take place. Iron carbide, cobalt carbide, etc. are formed and then we take this melt and quench it down; and while we quench it down, all kinds of reactions take place. The graphite which was dissolved in molten iron crystallises out and there are phase diagrams which describe the preparation and production of steel so that any little bit of change in the temperature profile gives us a different type. Many times one anneals carefully at a certain temperature because one wants to establish in the final object a certain equilibrium state of the various phases and in exactly the same manner it is done here. By extruding, spinning, casting and any kind of deformation of a polymeric material, we aim at the establishment of a certain ratio of the three possible phases, namely solid, rubbery and liquid, and the great advantage which we have in this organic chemical metallurgy over the standard metals is that we have the rubbery phase. In metallic state unlike in organic chemicals there exists no rubbery phase. Even if it does, it exists at very high temperatures. But we have in the case of polymers roughly in the range between −50°C. and + 150°C. So to make a nylon tyre cord, the nylon is spun and stretched, as much as possible and then it is annealed back and given another stretch, and eventually it is obtained at a certain temperature under tension. This, however, ensures that practically all the material will be in this rigid state. Because the modulus of the X-ray diagram and the density of the completely crystalline nylon are known, by measuring the density of the X-ray diagram and modulus of the tyrecord finally made, we can see if really 100 per cent crystalline material has been obtained or not. Well, in the case of tyrecord, it comes up to about 80%. Then what else should we do? Certainly we should have some rubberiness. In a yarn, which is used in the tyrecord, we would certainly like to have some elasticity because this elasticity will help us to get a good road life for our tyrecord. So, an ideal nylon tyrecord would probably be one which has 85 per cent of the material in the crystalline state and 15 per cent of the material in the rubbery state. But we do not want a nylon tyrecord to be plastic. Because, if it is plastic, it is going to flow; it is going to creep. But unfortunately, as is probably well known, there is always a certain amount of material, say, 5 per cent which still remains in this state. In other words, some volume elements of the chains are still in such a conformation. They actually are of this type and that causes the flat spotting and that causes the inflation loss and that is the reason why one still tries to find better and better production methods of nylon tyrecord in order to completely eliminate the plastic constituents. Cross-linking would do it and one of the ways of improving nylon tyrecord in respect of flat spotting is actually to cross-link the material. However, to make a nylon for stockings, evidently 90% of it in the crystalline phase is not needed. It will be very hard and unpleasant to wear. It is necessary to have it at 75%. For elasticity, 15% of this will be sufficient. In a stocking or any kind of knitted goods we want plasticity, because we want in the heat setting process, the bends on the fabric to be stabilized. Hence, if we ask how good a fibre nylon is, then the answer can be only given in extremely general terms. If an answer is needed in respect to the given application, it is necessary to find out if it is possible to bring nylon by certain degrees of stretching, annealing, etc. in such a kind of blending of these 3 types of phases that it does a good job in respect to•this application. Hence the art of spinning, casting or moulding, in other words, the entire technology of high molecular weight materials is based on these three phases- the solid, the rubber and the plastic phases. On top of the large variety provided by organic chemistry through different monomers and copolymers and that of the additional variety provided by physical chemistry through stereoregulation and cis-trans isomerisation, we have additionally the possibility to put a very large number of different characteristics by blending into a given material an appropriate mixture of these three phases. The rubbery phase is only got from large flexible molecules. The qualitative correlation to this quantitative aspect has been worked out in very great detail and in fact the start of all of it was a book which Dr Alfrey wrote on 'The mechanical behaviour of high polymers'. The quantitative interpretation of this approach is as follows. We recognise the fact that polymeric materials are in this sense mixtures of liquids and solids; sometimes everything is a solid and sometimes everything is a liquid and sometimes we have a liquid with an overall solid structure. The ideal solid is characterized by the graph [Fig. 12]. If we plot elongation against time and at a

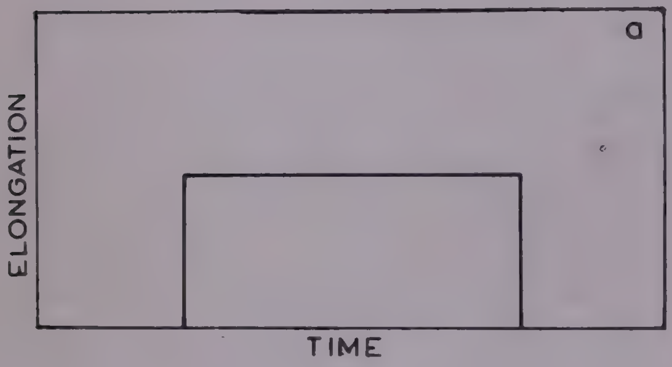


FIGURE 12

Relationship between time and elongation for a perfect solid

certain point we put a load or stress on our material, it will immediately jump to a certain length, it will stay at this length and as we unload, it will jump back again. That is the creep curve of an ideal solid, instantaneous elongation upon loading, complete equilibration with the load, instantaneous return upon unloading; all the energy is stored in the system. Now the equation for this kind of behaviour is very simple. The elongation is given by the stress divided by the modulus $El = \frac{S}{G}$, where the modulus G is a quantity which represents the reluctance of the material to deform. In other words, modulus is the resistivity. This tells how strongly the material resists deformation. The larger the modulus, the more rigid is the material and therefore, it is in the denominator. An appropriate illustration for such a behaviour is a steel spring which upon loading jumps readily and upon unloading goes back. The material of this type is called a Hookian solid because Prof. Hook established the fact that quartz, steel, etc. do behave like that. Now in the case of an ideal liquid, if we plot elongation versus time [Fig. 13] at the beginning of loading the material starts to elongate proportional to time and upon unloading nothing happens. A viscous liquid which does not run away under the influence of gravity, like pitch or polystyrene melt, keeps on elongating with time, it flows and if we stop pulling, it certainly is not going to come back so that the elongation now

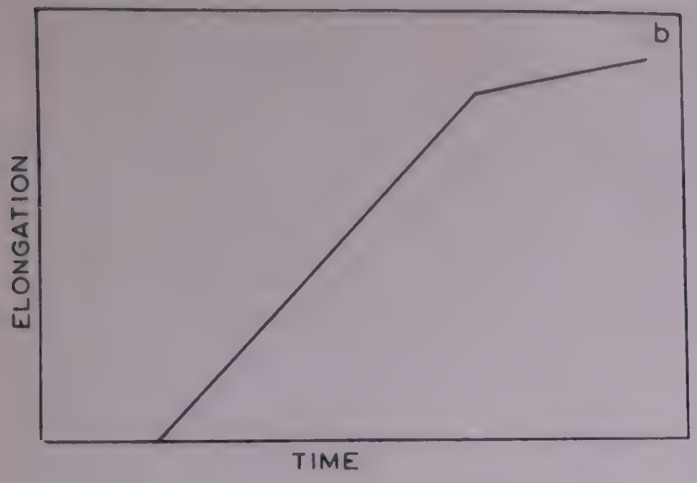


FIGURE 13

Relationship between time and elongation for an ideal liquid

is given by stress divided by viscosity, times t, $\cdot El = \frac{S}{\eta} t$ and here viscosity again is a quantity which describes the reluctance of the material to flow, a quantity of the resistivity type just like the modulus. So it is again in the denominator. An illustration [Fig. 14] for this behaviour is a little cylinder with a piston

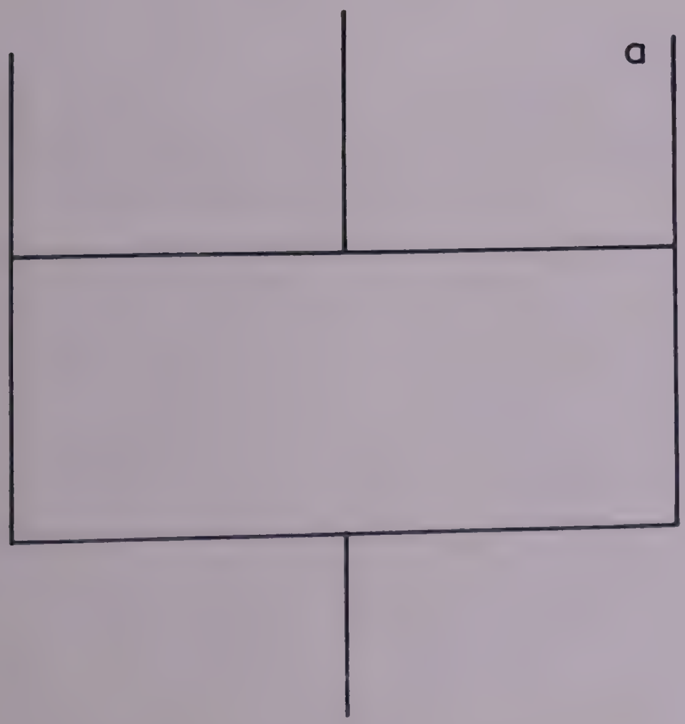


FIGURE 14

Dash pot

which supposedly moves in a liquid of a certain viscosity and this gadget has been called dashpot. The spring is the description for a Hookian solid and a dashpot is the description for a Newtonian liquid because this is a liquid as first described by Newton. The spring and dashpot mechanisms were combined into one by Maxwell. After the discoveries of Faraday, electricity became a very interesting form of energy and with it of course came the necessity to conduct it away in wires. So the technology of making wires started to develop at that time and with it of course the embarrassment that these wires have a certain tendency to creep and Maxwell started to study the creep characteristics of wires of all kinds, specifically of copper wire. He found that if we take a copper wire, put a weight on it, then what happens is represented in Fig. 15. The wire first jumps a certain extent and then keeps on flowing and if unloaded, it jumps back just exactly as much as it jumped at the beginning and the rest is a permanent set. This is very easy to handle because that is nothing but a linear superposition of the behaviour of a solid $(\frac{S}{G})$ which is recoverable, plus S divided by viscosity, times t, $(\frac{S}{\eta}t)$ which is the irrecoverable part and in the picture we have a spring and the dashpot in series [Fig. 16]. This is called a Maxwell element. So in order to describe the behaviour of a material like lead or copper, we cannot get away either with the elasticity or modulus, we need both modulus and viscosity. Now it is true that the viscosity in the case of copper is very high, so that actually the creep is low; and particularly if the copper is hard-drawn, the creep is very low but in the case of lead, the creep is quite high. Whenever a wire is made specifically for the purpose of conducting away electricity, it should be seen that it consists essentially of a spring or Hookian solid i. e. we remove all the amorphous parts in the copper and get only the oriented crystals.

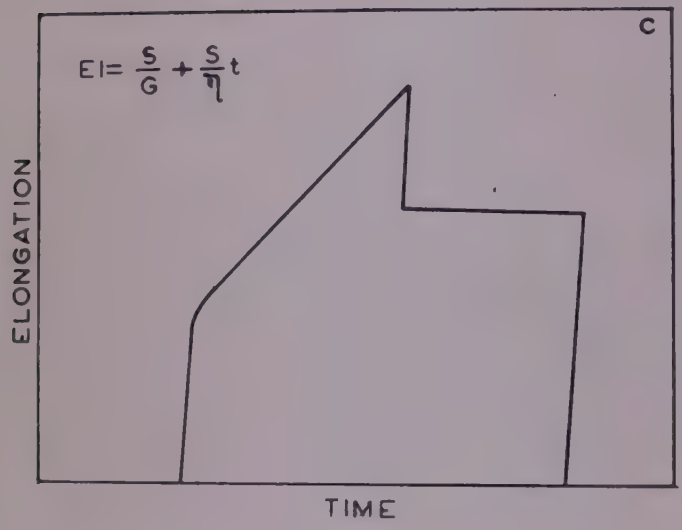


FIGURE 15

Relationship between time and elongation for loading and unloading of a copper wire

Now about the same time another physicist, Voigt, in Germany, was interested in the study of the mechanical behaviour of rubber. When a piece of rubber is taken and a weight is put on it, it elongates and when it is unloaded, it comes back. From this, situation which is graphically represented in Fig. 17. it can be seen that instead of getting a quick recovery, which is got for an ideal solid, we get a delayed response. Instead of getting a complete instantaneous

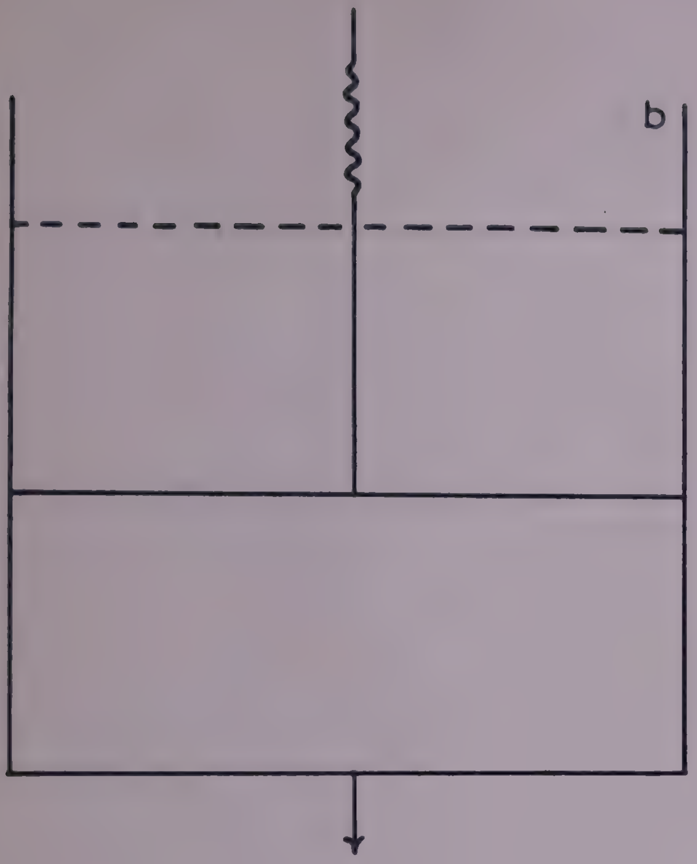


FIGURE 16

Dash pot and spring in series

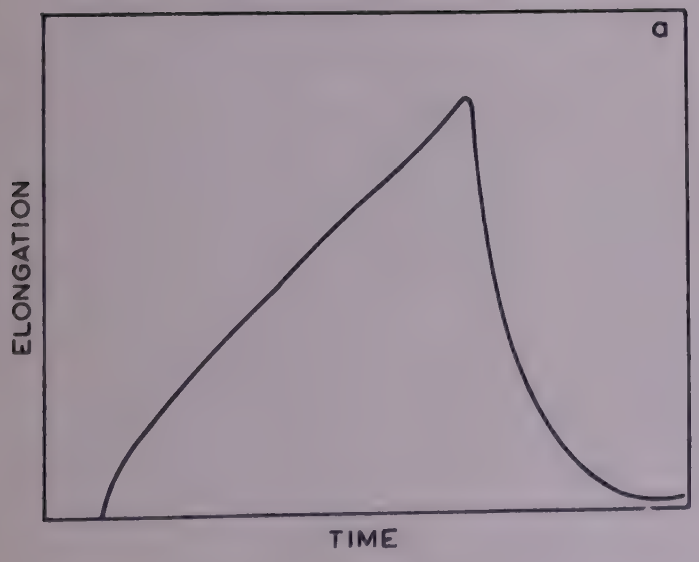


FIGURE 17

Relationship between time and elongation for a piece of rubber storage, a delayed storage is got,though it is complete return of energy. Nothing is dissipated. If a spring and a dashpot connected in parallel [Fig. 18] are taken and pulled, the spring would like to elongate immediately, but the dashpot does not allow it. It takes time for the dashpot to move. Hence the sudden jump is smoothed out to a curve and then when relaxed, the spring is going to pull the system back, but again since the dashpot only allows slow motion, it cannot jump back but it creeps back. So we have the phenomenon of delayed elasticity

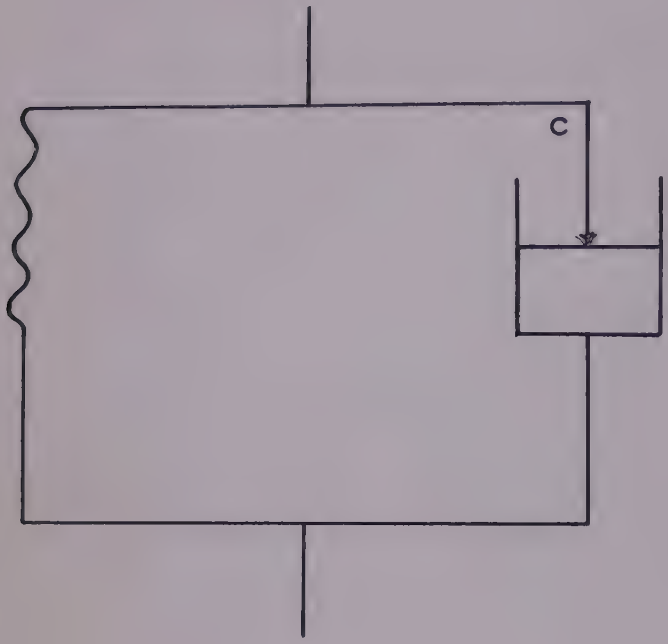


FIGURE 18

Dash pot and spring in parallel

and again we need a modulus and a viscosity in order to describe this kind of phenomenon. One can also write down a simple equation to have a quantitative mathematical representation. Now what Prof. Alfrey recognised in his work and what he eventually concluded in his book is that for the description of a polymeric material, it is not possible to get away either with a Maxwell element or with a Voigt element, but both are needed. This creep curve has a permanent set as most creep curves have, has a rather sharp initial jump and has also the curvature as shown in Fig. 19. Again, in order to describe completely the behaviour of polymeric materials, we need two moduli G_1 and G_2 and we need two viscosities η_1 & η_2 [Fig. 20]. This corresponds completely to our qualitative scheme, in which we had the internal Brownian motion and the external Brownian motion forbidden at low temperatures- in the solid-rigid range (-iBM &-eBM). We have internal Brownian motion allowed but the external Brownian motion forbidden in the rubbery range (-iBM & -eBM). And we have both internal Brownian motion and external Brownian motion allowed in the liquid-plastic range, or melt range, or it may be called a plastic range to indicate the high viscosity (iBM & -eBM). A negative sign means transferring stress, storing energy, so the negative sign corresponds to the springs. The + sign means motion, either segmental motion or motion of the molecules as a whole. They dissipate energy and they correspond to the dashpot. Now it can easily be seen, that when we start at the bottom, the dashpot gives us the permanent set, because permanent set is caused by the motion of entire macromolecule along

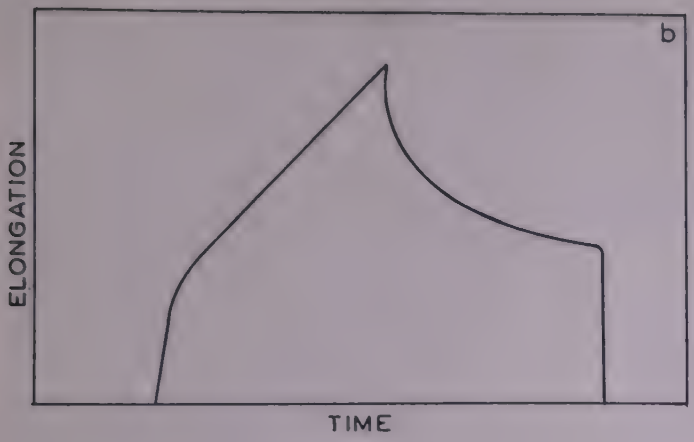


FIGURE 19

Relationship between time and elongation for a polymeric material

over each other before they permanently, irreversibly change their conformation. The segmental motion which delays the elastic response is the dashpot with η_2 (viscosity). The springs responsible for the high modulus and for the low modulus are G_2 and G_1 [Table 2]. This is a rather clearcut correspondence between the qualitative picture in the form of a scheme and the quantitative formulation in the equation. Dr. Alfrey himself described in his book, a large number of 50-60 creep curves of nylon, cotton, rayon, etc. and has evaluated them.

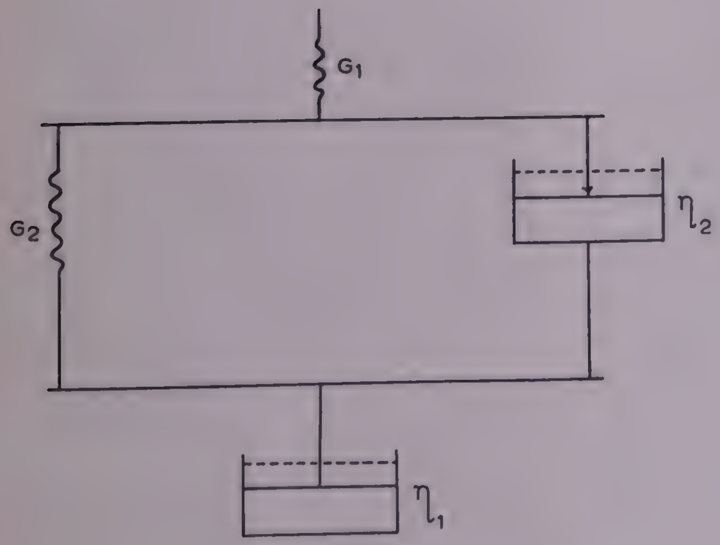


FIGURE 20

Dash pots and springs in series

Table - 2 Qualitative Scheme of Brownian Motion

Solid, Rigid range	Rubber	Plastic
G_1 i B M –	i B M +	i B M + η_2
G_2 i B M –	e B M –	e B M + η_1

Dr. Leaderman in his book has actually evaluated several hundreds of creep curves in terms of the four parameters, two moduli and two viscosities- superposition of the spontaneous response, delayed response and very long time creep and when that was done, it was evident that these four quantities sometimes are sufficient and sometimes are not. What Prof. Alfrey has proposed is that when we really want to take care of all the details of responses of a material, then we have to realise the following. First there is a very rapid response which comes from the fact that a nylon crystal is very hard and eventually behaves like a steel spring. Next comes a whole set of amorphous areas, in other words, somewhere the segments are more crowded than somewhere else, so actually one cannot get away with one Voigt model but several such models are required. At the end there is a permanent creep, so that actually now there is high viscosity and these viscosities all get less and less - get smaller and smaller and between the very high modulus of instantaneous response and very high viscosity of very long range deformation, there is a spectrum of Voigt models. It is called relaxation spectrum as it tells us how any material responds as more and more time is given to it. The whole sense of it is a mechanical spectroscopy. In reality, if we elongate a material for a micro-second, it would not elongate very far because only very rapid mechanisms, such as breaking of a valency bond or stretching of a valence, can respond so fast. When it is given a certain time, say, a second, certainly rotations can take place in the segment of the amorphous areas and a new mechanism comes into play. This mechanism provides additional elongation and giving further time, say, a minute, longer segments will unfold. On allowing more time, say about one year, the whole thing will flow. Macromolecular material is like an orchestra which has a large number of characteristic frequencies with which it can respond to a deformation. Now this tells us how a material behaves as we give it more and more time to modulise its different tense mechanisms against elongation. If a brutal jerk is given, it will break because all these mechanisms which would allow to expand, say upto 100%, cannot get into play because they are too slow. If the same force is used for a long time, this will not break and it is going to elongate. This is the importance and interest of the relaxation spectrum that we can correlate with molecular events. We know that the high modulus corresponds to deformation of the crystals and the low modulus to the segment motions and since segments can be long or short, we have a whole spectrum of the segmental motions representing the spectrum of Voigt modulus. Well, for a mathematical formulation of this, very fortunately no work was necessary at all. It was all worked out already because this is exactly the same thing mathematically as the theory of electric circuits. In circuit theory, there are also elements which dissipate the energy, namely resistance. They correspond to the dashpots. And there are the elements which store electric energy, namely capacitors and they correspond to the spring and in any radio or television sets, we have this. Somehow, certain frequencies are built in and we can change them. Now, only we have put in springs and dashpots, that is all.

In the case of construction of an electric circuit, we start putting in the springs and dashpots and we figure out also the characteristics of the system, depending on the current flowing through it when we put in a certain voltage. Thus we start ourselves putting these things in and end up with a predetermined circuit characteristic. This curve corresponds to the circuit characteristic and from this creep curve, we have to work back to the necessary elements which we need in order to get their kind. So the electrical engineer works synthetically from the elements to the final behaviour whereas Dr. Alfrey had to work analytically from the final behaviour back to the elements. Well, meanwhile, as is well known this has developed into a branch of physics of large molecules. To what it amounts in the end is that we understand now why a polymeric material has certain responses, certain immediate responses and certain delayed responses. We want delayed responses just as much as immediate responses, say from milliseconds to hours. Our case is a little bit more complicated than the electrical case because when the polymer is worked, by milling for example or during elongation, crystallisation takes place. In other words, the boundary lines between phases are not static, they move around. But very fortunately it is not the case with a radio set. If we buy a radio, we put it with a definite arrangement of springs and dashpots, but one can of course, as at the beginning, work out such conditions where there was little or no dynamic tests, there was no additional change in degree of crystallinity. A little experiment which indicates the tremendous influence of orientation on mechanical behaviour can be demonstrated by taking a polyvinyl alcohol yarn which consists of 50 filaments- rather a strong yarn. Yarns of this type have been used for all kinds of things. It is well known that polyvinyl alcohol as such is soluble in water because of the many hydroxyl groups it has. So we have an oriented drawn polyvinyl alcohol filament consisting of crystalline domains and amorphous domains also. Its solubility in water is caused by the fact that water rushes into the amorphous domain, starts dissolving and the whole structure goes to pieces. If a small stress is applied, say 50g., this is enough to increase the lateral hydrogen bonding between the amorphous domains so that the material is not dissolved. This can be shown by putting the yarn in water which is almost boiling (92°C) in such a manner that the filament is under tension and it can be seen that it does not dissolve. The part not under tension is dissolved immediately, but the filament is still there. This can be put in and taken out but as soon as the bottom is touched by the weight the yarn is relaxed and it dissolves. A test sample of syndiotactic polyvinyl alcohol however does not dissolve at all even when relaxed, and will remain undissolved, regardless of what is done because of the syndiotactic structure. In the syndiotactic type, the amorphous areas are, in any event, insoluble in water. They are not actually insoluble- in about 15 minutes, they will dissolve if acid or alkali is added they dissolve immediately but otherwise for the time being, it remains unaffected. Thus the vast difference between the behaviour of these two materials is seen and this shows how sensitive these materials are in respect to exact alignment of chains and improvement of this alignment by tension.

DISCUSSION

28. **Mr. N. V. Viswanathan:** I would like to know what the tackiness of a polymeric material in the rubbery state is due to?

Prof. Mark: Well, tack depends on low molecular weight constituents. So the so-called tack of rubber has to do with the fact that the rubber after milling contains some low molecular weight materials. So it is the characteristic of a plasticised system and a lot of chains give tack or a lot of the chain ends give tack.

Mr. Viswanathan: But it happens only when the polymeric material is in the rubbery state, why is it so?

Prof. Mark: Now tackiness has nothing to do with being a rubber. It is the true natural rubber which is tacky but there are many tacky substances which are not rubbers and many rubbery materials which are not tacky.

Mr. Viswanathan: Yes, polymethyl acrylate is tacky at room temperature.

Prof. Mark: Well, it just has its second order transition point at less than room temperature.

Mr. Viswanathan: In other words, it is also in the rubbery state at room temperature?

Prof. Mark: Yes.

Mr. Viswanathan: I just want to know why the tackiness is only in the rubbery state and not in other two states.

Prof. Mark: This (3rd liquid state) is just as tacky as the rubbery state e.g. molten polystyrene is extremely tacky. This (solid state scheme) is not tacky. You see, tackiness and adhesivity have to do with amorphous areas.

29. **Dr. R. V. Subramanian:** How exactly does one define tackiness?

Prof. Mark: Well, there have been a number of quite interesting articles where Dr. Bikerman has attempted to correlate tack with viscosity of the system and in certain cases, I think it is true. But it is such an ill defined phenomenon. The first question is "how do you measure tack?" Then the answer is "Well, I don't know". There are several proposals and they are in conflict with each other. As long as you cannot measure anything with reproducibility, it is very difficult to fit it into a quantitative scheme of considerations.

30. **Dr. N. D. Ghatge:** What about the tackiness of rosin?

Prof. Mark: Well, at sufficiently high temperatures, it is tacky.

31. **Dr. M. K. Gharpurey:** Considering the three phases of the polymeric materials, could you tell us about the course of specific heat as a function of temperature?

Prof. Mark: Well, you know that the heat content or specific heat of the system looks like in Fig. 21. The solid part, rubbery part and the liquid part are indicated. At the boundaries, there is a sudden change in the slope of the volume, heat content and so on. This is a 2nd order transition point and the specific heat becomes larger and larger, the more mobility there is provided for. In other words in the melt, it is largest.

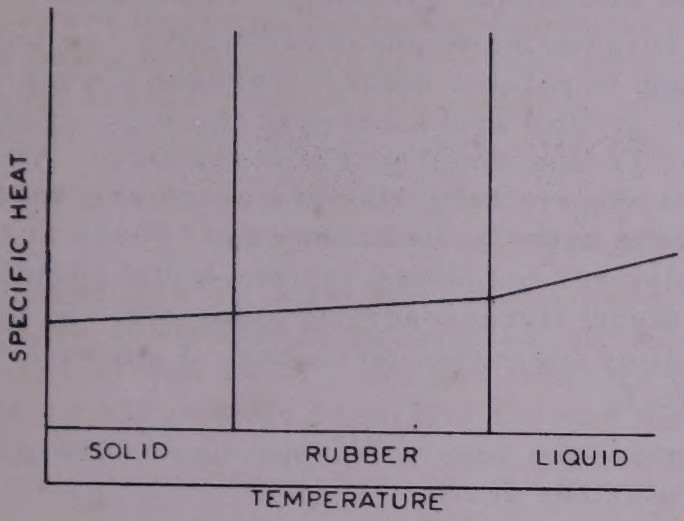


FIGURE 21

Specific heat as a function of temperature describing solid, rubber and liquid phases

32. **Mr. T. V. Subba Rao:** Has polarity got any specific effect on tackiness?

Prof. Mark: No, many polyhydrocarbons like rubber or polyethylene are tacky. It is the effect of temperature on it. You see, polyhydrocarbons are very tacky in the right temperature range.

Dr. R. V. Subramanian: In this connection, I want to mention the findings of Mr. B. C. Sekhar of the British Rubber Producers Research Association, Malaya, that the presence of a few polar groups viz., aldehyde groups are responsible for the tackiness of natural rubber. Synthetic rubber with the same percentage of cis 1-4 addition units and molecular weight distribution as natural rubber still does not have the tackiness of natural rubber and this would further indicate that the polar aldehyde groups present in natural rubber but not in synthetic rubber might be responsible for the tackiness of natural rubber. Could you elaborate on that?

Prof. Mark: Well, it all depends on what synthetic rubber you take; styrene-butadiene copolymer, it is 80 times more tacky than natural rubber.

Dr. Subramanian: I am referring to synthetic cis 1-4 polyisoprene.

Prof. Mark: You take a sample of natural rubber and another sample of synthetic rubber and you find that one is more tacky than the other. First of all it would be necessary to say whether molecular weight is same then molecular weight distribution is same.

But it is perfectly possible that if a few polar groups in natural rubber increase the tack, then polar groups would increase the tack. I am sure polar groups would increase the tack. As I said, there are synthetic rubbers which are specially made in order to be adhesives. Those are copolymers butadiene-styrene-vinyl pyridine, butadiene-styrene-acrylic acid, etc. So polarity certainly increases tackiness. I am sure it is currect.

33. Dr. G. R. Pathak: What are the superior properties of low pressure polyethylene due to?

Prof. Mark: The difference between low pressure/high density polyethylene and high pressure/low density polyethylene is due to branches. Normal polyethylene (high pressure) has many short and a few long branches, and is much less capable of crystallising than a material which is linear. So high density polyethylene has a melting point of 130°C. low density polyethylene has m.p. 110°C But this has nothing to do with stereoregulation. It is only due to linearity.

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